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EFFECT OF POLYMER STRUCTURE ON SOLUBILITY, COMPATIBILITY AND THERMAL STABILITY

A Dissertation Presented

by

Miomir Blagoje Djordjevic

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1983

Polymer Science and Engineering

EFFECT OF POLYMER STRUCTURE ON SOLUBILITY, COMPATIBILITY AND THERMAL STABILITY

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Miomir Blagoje Djordjevic

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To my parents, for their love.

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ABSTRACT

EFFECT OF POLYMER STRUCTURE ON SOLUBILITY, COMPATIBILITY AND THERMAL STABILITY

February, 1983

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Changes of the chemical shifts in the nuclear magnetic resonance, NMR, of the solute, induced by specific intermolecular interactions, IMI, such as hydrogen bonds and dipole-dipole interactions, are separated from those induced by the nonspecific, dispersive, IMI applying Rummens method. Specific IMI have been detected for several compounds of low molecular weight and for poly(vinyl methyl ether), PVME, polystyrene, PS, poly(2,6-dimethyl-1,4-phenylene oxide), PPO, and poly(vinyl chloride), PVC, with different solvents. By extrapolating these findings, it was possible to understand the mechanism of the IMI in the two compatible polymer blends: PVME-PS and PPO-PS. In addition, effects of some solvents on the homogeneities of cosolution-cast PVME-PS blends have been explained.

For some organic compounds, cohesive energy density, CED, within a homologous series changes linearly with a single material parameter, $g^2 = [(n^2-1)/(2n^2+1)]^2$, reflecting the intensity of the Onsager reac-

tion field; n is the refractive index of the compound. This correlation has been found for n-alkanes, 1-n-alkenes and n-alkyl benzenes (all having only dispersive interactions), for methyl-n-alkyl ketones (with dipolar interactions), and for linear alcohols (forming hydrogen bonds). Correlation for n-alkanes, extrapolated to corresponding g^2 is in good agreement with CED for polyethylene.

Thermodegradation properties of poly(ortho chloro styrene), POClS, and PS show several differences, the most pronounced one being in the pattern of the molecular weight change at moderately high temperatures when neither of the polymers exhibits any weight loss. These differences are explained as the effect of the ring substituent on the conformational mobility and free-radical activity of POClS.

PREFACE

Effects of repeat unit structures on the macroscopic physico-chemical properties of polymers are the object of continuous study. As our ability to define and measure the macroscopic properties of polymers improves, the need expands for better understanding both of their microscopic properties and the relationship between the macroscopic and microscopic properties. It is particularly important to understand how chemical structure affects polymer solubility, its compatibility with other polymers and its thermal stability. This thesis reports on efforts to understand better these relations.

The thesis is divided into fourteen chapters, which may be further separated in three sections. First section, composed of Chapters I to XII, reports on the characterization of the intermolecular interactions, by observing the small changes in the specific resonant frequencies in nuclear magnetic resonance spectra. These characterizations have been performed on compounds of low molecular weight, oligomers and on polymers. The aim of this study is to understand the intermolecular interactions between the polymer repeat unit and the neighboring molecules, for the purpose of understanding the mechanisms leading to polymer solubilities and compatibilities.

Chapter I reports the historical development for the application of the nuclear magnetic resonance as a probe for the intermolecular interaction. Chapter II introduces the objectives of the study and the experimental procedures which are used for their realization. Chapters III to VII report on the studies of the intermolecular

interactions among several compounds of low molecular weights. These compounds of low molecular weights are either models for polymer repeat units or solvents for polymers of interest. Their intermolecular interactions help understand the changes brought by the interactions on both the repeat unit and the solvent molecule. Chapters VIII and XI are reports on the studies of the intermolecular interactions in the solutions of some polymers and oligomers. These results may explain polymer solubilities and compatibilities and the effect of solvent on the compatibility among polymers. Chapter XII outlines the needs and objectives for further studies in the area covered with the first section.

Second section contains only Chapter XIII. It reports about a new, very general relationship which has been found to exist between the cohesive energy density and the intensity of the Onsager reaction field in some organic liquids.

Third section contains Chapter XIV and it deals with a parallel study of the thermal and thermo-oxidative degradation of polystyrene and poly(ortho chloro styrene).

Each chapter, except Chapter II was written as a self-standing report concerned with one narrow subject, discussing the previous work and drawing conclusions related to it. Chapters I and VIII are parts of the paper submitted to the journal "Macromolecules". The content of the Chapter IX was presented at the second symposium on Polymer Blends in Montreal, Canada, April 20, 1982 and submitted for publication in "Polymer Engineering and Science - Polymer Topics". The major

part of the Chapter X was presented at the national meeting of the American Chemical Society in New York, August, 1981. The Chapter XIII, appears in the book "Macromolecular Solutions - Solvent-Property Relationships in Polymers" edited by R.B. Seymour and G.A. Stahl, published by Pergamon Press, New York, 1982.

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C H A P T E R I

CHEMICAL SHIFT IN NUCELAR MAGNETIC RESONANCE AS A PROBE FOR THE DETECTION AND IDENTIFICATION OF INTERMOLECULAR INTERACTIONS

Introduction

One of the most advanced fields of polymer science is the study of thermodynamic phenomena reflecting intermolecular interactions, IMI, in polymer solutions (1-3). Lacking, however, is a systematic analysis of the specific mechanisms of the IMI engaging the repeat unit of the polymer. A more detailed understanding of those molecular mechanisms can thus improve our prediction of polymer solubility and of polymer-polymer compatibility. To achieve this goal it is necessary to collect information on the IMI which may be caused by the structural group in the chain repeat unit and to understand whether certain polymer repeat units enter into only one or into several simultaneous IMI.

The IMI are known to affect the NMR spectra of organic compounds (4-8), and changes in a polymer's nuclear relaxation times (9-11) are frequently interpreted as an indication of the IMI. Solvent induced changes in NMR chemical shifts, SIS, also reflect IMI between the compound under observation and the solvent. SIS of polymers have been used to identify the interaction between poly(methyl methacrylate) and aromatic solvents (12,13). However, there apparently has not been any more studies of interactions for other polymer-solvent and polymer-

polymer pairs. An SIS needs to be reported relative to the chemical shift of the compound under observation in some reference state. Usually, this has been the compound in solution in a selected nonpolar solvent (such as CCl_4 (14) or cyclohexane (15)) or in the gas phase (16). Some IMI such as dipole-dipole interactions (17,18), hydrogen bonds to n-electron donors (8,19,20) and hydrogen bonds to π-electron donors (21-24), cause SIS with characteristic directions and intensities. In addition it has been demonstrated that intensities of IMI influence the intensities of the related SIS (25-27). However, by referencing all SIS to a single state it is not possible to separate the contribution to SIS caused by a simultaneously occurring dispersive interaction (18,19). This, in turn, prevents one from determining the correct orientation and the intensity of SIS induced by the "specific" interaction (29). A large effort, both theoretical and experimental, has therefore been made to determine this contribution of dispersive IMI to SIS (29).

Effect of Dispersive Intermolecular Interactions on Chemical Shifts

The theoretical analysis of the relationship between IMI and SIS is most often done by considering the effect of the electric field on SIS (30-39). The electric field acting on a nucleus results from the presence of the surrounding medium polarized by the molecule (40). Buckingham (32,33) suggested that its intensity on a polar molecule may be approximated (41) by the intensity of Onsager reaction field, $\underset{\sim}{R}_O$ (38,42-44).

$$\underset{\sim}{R}_o = \frac{\underset{\sim}{\mu}_1}{a_1^3} \left(\frac{\varepsilon_2 - 1}{2\varepsilon_2 + n_1^2}\right) \qquad \text{(I-1)}$$

In this equation, μ_1 is the dipole moment of the solute, occupying a cavity with radius a_1 and having refractive index n_1 in its pure state; ε_2 is the dielectric constant of the solvent. Linder (34) extended this concept to the case of a nonpolar solute, with fluctuating dipoles, $\underset{\sim}{m}(\nu_i)$, creating the fluctuating reaction field, $\underset{\sim}{R}^*$

$$\underset{\sim}{R}^* = \frac{2\underset{\sim}{m}(\nu_1)}{a_1^3} \left(\frac{\nu_2^2}{\nu_2^2 + \nu_1^2}\right) \left(\frac{n_2^2 - 1}{2n_1^2 + 1}\right) \qquad \text{(I-2)}$$

Here n_2 is the refractive index of the solvent and ν_1 and ν_2 are fluctuation frequencies characteristic of the solute and solvent, respectively. The concept of the uniform reaction field in a spherical cavity is valid only for small spherical molecules. The real intensity of the electric field on a large, nonspherical molecule depends also on its shape (42-44) and its chemical structure (45-47). In a complex molecule each bond may behave as a dipole inducing an electric field (47,48). Depending on the bond's character, this field may be stationary, $\underset{\sim}{R}_o$, or fluctuating, $\underset{\sim}{R}^*$. The resulting complex field (45,46),

$$\underset{\sim}{R}' = \underset{\sim}{R}_o + \underset{\sim}{R}^* \qquad \text{(I-3)}$$

has a different intensity, $\underset{\sim}{R}''$, at every nucleus of the molecule (45-47)

$$\underset{\sim}{R}'' = k_i \cdot \underset{\sim}{R}' \qquad \text{(I-4)}$$

where k_i is a constant accounting for this field nonuniformity.

In very large, nonspherical, as well as in chain-like molecules, however, even the concept of the single field, albeit the complex one, cannot be applied any more (48). It is apparent that in such cases one must consider the reaction field on one segment of this large molecule only.

The dispersive interaction arises from the coordination of charge fluctuation between neighboring molecules (49,50). The frequency of such fluctuations is too high for permanent dipoles to follow (45,46,51), so this kind of interaction does not cause orientation (49). Its physical character in the liquid is thus the same as in the gas phase (37,52). By analogy, chemical shifts induced by this interaction may be expected to change regularly between the gas phase and van der Waals solutions. Several early efforts to find a correlation of chemical shifts from both the gas phase and solutions with a single material parameter have been only partly successful (52-55).

Apparently, most successful in defining this relation was Rummens (49,50). Theory indicates that the chemical shift induced by a dispersive interaction should be proportional to the average square of the electric field (31-33,51,56). In the case of a dispersive interaction this is the time average square of the complex field (45,46) which, in turn, is equal to the average square of the fluctuating field defined by Linder (Equation 2) (34). Combining those

theoretical findings with earlier experimental results (33,52,53), Rummens has demonstrated that proton chemical shifts of gaseous CH_4 and of CH_4 dissolved in different solvents are linearly correlated with the parameter $[(n_2^2-1)/(2n_2^2+1)]^2$ of the solvent ($n_2$1 for a gas).

For small spherical molecules (51,57) the change of the chemical shift induced by the dispersive interaction, δ_W, is

$$\delta_W = - \frac{KB}{a_1^6} \cdot \alpha_1 \cdot I_1 \cdot \left(\frac{n_2^2 - 1}{2n_2^2 + 1}\right)^2 \left(\frac{1}{1 - q^2}\right)^3 \qquad (I\text{-}5)$$

where α_1 and I_1 are the polarizability and ionization potential, respectively, of the solute. K is the constant compensating for the errors in applying the theoretical expression for the electric field on the permanent dipole (Equation 1) (40) to the case of a fluctuating dipole (Equation 2) (34), and compensating for the nonuniformity of the electric field at the molecule (Equation 4) (45,46). The proportionality factor, B, is relating δ_W and the average square of the electric field at the nucleus (51). It may be expected that a_1 corresponds to the van der Waals radius of the molecule, Rummens, however, finds that it cannot be well correlated with any of the parameters characterizing the size of the molecule (51). The intensity of the chemical shift is higher if the nucleus is nearer to the molecule of the solvent. This is in agreement with findings of Laszlo and Musher (47) but it is a departure from the simply formulated concept of an Onsager cavity (40). This deviation is expressed through the site factor $(1-q^2)^{-3}$ (51) where $q=d/r_{12}$; d is the distance between the molecule's center of mass and the observed nucleus and $r_{12}=r_1+r_2$ where

r_1 and r_2 are van der Waals radii of the solute and solvent molecule, respectively.

It was later demonstrated that ^{13}C chemical shifts for solutions of small and large nonpolar molecules (18,58-61) and for solutions of different polar molecules (18,60,61) show similar correlations.

As it was mentioned earlier for large nonspherical and chain-like molecules, different intensities of reaction fields may be considered for different nuclei of the molecule (45-48). For large molecules dissolved in nonpolar isotropic solvents (51,58-60) the change of the chemical shifts, δ_W, for each nucleus is expressed as

$$\delta_W = S_j \cdot g^2 + C \qquad \text{(I-6)}$$

where $g^2=[(n_2^2-1)/(2n_2^2+1)]^2$ and C is a constant. The slope of this line (van der Waals line, VDWL), S_j, reflects the sensitivity of the structural group, containing the observed nucleus, towards dispersive interaction, i.e. towards the fluctuating electric field. There are no reports concerning the intensity of the electric field on a nucleus in such a molecule. However, an analogy may be drawn between a small molecule and a structural group in the large molecule (48). One may consider that characteristic properties, such as polarizability and ionization potential, determine the sensitivity of the structural group to the influence of the solvent as well. The size and shape of the Onsager cavity and the site factor cannot be determined. However, these parameters would depend on the accessibility of the structural

group to the solvent molecule, which then influences the value of S_i (60).

The VDWL may be considered a general pattern for SIS caused by dispersive interactions. However, ^{13}C chemical shifts change somewhat differently from those of the attached protons. Extrapolation of their values obtained in van der Waals solvents to $g^2=0$ yields chemical shifts, which are downfield from those determined for the gas phase. A similar effect has been reported for ^{129}Xe NMR chemical shifts (62). The full explanation of this phenomenon has not yet been given (56-58,62).

It is assumed that the NMR chemical shift between the gas phase and VDWL at a certain g^2 corresponds to the dispersive component of the IMI between the solute and a solvent with this g^2 (28). The VDWL can thus be used as a "base line" for the determination of the SIS induced the "specific" compound of the IMI, now seen as deviations from the VDWL.

This offers a very convenient method for the experimental detection and identification of the specific IMI.

Dipole-Induced Dipole Interactions and Chemical Shifts

When Rummens plot is applied for polar compounds a concern exists about the possible effect of dipole-induced dipole interaction on the position of VDWL. The effect of dipole-induced dipole interaction NMR chemical shift in general was first analyzed theoretically by Buckingham (32) and the effect of the polar solvent on the chemical

shift of a nonpolar solute, δE^2, has been analysed by Raynes, Buckingham and Bernstein (33). Rummens and Mourits (57) as well as Cans, Tiffon and Dubois (60) have studied this problem experimentally. They find that the effect of this interaction in liquids can be negligible for nonpolar solute. This is in an agreement with the theoretical findings of Montgolfier that permanent dipoles in the surrounding molecules of the solvent cannot relax fast enough to follow the high frequency of the fluctuating moments in the nonpolar molecule of the solute (45,46,51). This, in turn, causes their average contribution to the complex field on the solute to be near zero. As the result, the only field which can affect the nonpolar solute is the fluctuating field caused by its own charge fluctuation (34,35). It will be modified only by macroscopic dielectric properties of the solvent.

When a polar molecule is immersed in the nonpolar solvent Buckingham (32) finds the dipole-induced interaction to cause a change in chemical shift of its protons, δ_E, which can be defined as:

$$\delta_E = k_1 \underset{\sim\sim}{R_Z} + k_2 \underset{\sim\sim}{R_O}^2 \qquad \text{(I-7)}$$

Where $\underset{\sim\sim}{R_O}$ is the intensity of Onsager's field (see Equation I-1) on the nucleus and $\underset{\sim\sim}{R_Z}$ is its projection on the C-H bond. This relation can be approximated so that the change in chemical shift is proportional to the intensity of the field. A similar theoretical conclusion has been reached by Batchelor (48,64). Tiffon and Dubois (18) have reported the experimental evaluation of δ_E for acetone dissolved in nonpolar solvents including n-alkanes, nC_6F_{14} and CCl_4. They find

that neither the chemical shift of methyl nor the one of carbonyl carbon show any deviation from VDWL which can be correlated with the parameter $(\varepsilon_2-1)/(2\varepsilon_2+n_1^2)$ (see Equation I-1). Similarly, no evidence has been found indicating that dipole (solute)-induced dipole (solvent) interaction affects the chemical shifts of alkyl substituted ethylenes dissolved in nonpolar solvents (60). Although those experimental findings do not agree with the theoretical predictions (32,33) they are in accord with the reports that dipole-induced dipole interaction makes only a small contribution to the total energy of IMI (28,65,66). In relation to the qualitative analogy which has been demonstrated between the effects of the dispersive interaction on the UV and on the NMR spectra (52) it is interesting to note that dipole-induced interaction has been found to have only a very small effect on UV spectra (67).

Bonding Intermolecular Interactions Affecting Chemical Shifts

The effect of the dipole-dipole interaction has been analysed experimentally by Cans, Tiffon and Dubois (18). When acetone is dissolved in polar solvents chemical shifts of its carbonyl carbon show the deviation from VDWL δ_d, which obey the simple relation:

$$\delta_d = C \cdot \frac{\mu 2}{(V_1^{1/3} + V_2^{1/3})^3} \qquad \text{(I-8)}$$

Here μ_2 is the dipole moment of the solvent, and V_1 and V_2 are molar volumes of the solute and the solvent respectively. Contrary to the

theoretical expectations (32,33) chemical shifts induced by dipole-dipole interaction were composed of only the dispersive and dipole-dipole contribution and did not have any dipole-induced dipole originated component (18).

The carbonyl group in acetone is expected to form hydrogen bonds with such proton donors as water, methanol, haloforms and dihalomethanes. When acetone is dissolved in those solvents its carbonyl carbon shows downfield deviation from VDWL which are considerably stronger than those induced by dipole-dipole interactions. There were no reports of further characterization of those deviations (60). It has been reported earlier (68) that when electron donor, hydrogen and the attached carbons are colinear the hydrogen bond may induce an upfield change of the chemical shift for both the hydrogen and its attached carbon. None of those chemical shift changes has been analyzed in terms of deviation from VDWL.

When 1,1-dialkylsubstituted ethylenes are dissolved in chlorinated solvents their substituted sp^2 carbons show a deviation downfield from VDWL indicating deshielding (59,60). At the same time however the unsubstituted, vinylic, sp^2 carbons show pronounced deviations upfield indicating the increased shielding. It was found that those deviations are not induced by dipole-dipole nor dipole-induced dipole interaction (60). However the deviations from VDWL induced by the same chlorinated solvent on unsubstituted carbons in different 1,1-dialkyl substituted alkanes correlate very well with the densities of π-electron charge at those carbons determined by

molecular orbital calculations (60). This behavior has been attributed to the n-π interaction between the free electron pairs in halogens and π-orbitals in substituted ethylenes (60). Although the number of reported works applying the Rummens plot to analyse IMI in terms of deviations from VDWL is very limited (18,58-63) already mentioned experimental results suggest that Rummens plot offers one advantage over the approach by Laszlo and Speert (52) for both identification of specific interactions and the estimate of their relative intensities.

Nonbonding Intermolecular Interactions Affecting the Chemical Shifts

In order to exploit fully the possibilities for the characterization of the bonding IMI which are brought by the Rummens plot, considerable attention has to be paid to the SIS induced by nonbonding IMI. In an uniform magnetic field, Ho, as the one applied by NMR spectrometer, an induced magnetic moment, $\underset{\sim}{n}$, is formed on the molecule.

$$\underset{\sim}{n} = \underset{\sim}{\chi} \cdot \underset{\sim}{Ho} \qquad \text{(I-9)}$$

$\underset{\sim}{\chi}$ is the molecular diamagnetic susceptibility which, depending on the structure of the molecule may be considerably anisotropic (69,70). As a consequence the induced magnetic moment, $\underset{\sim}{n}$, is always in a fixed orientation relative to the principal axis of the molecule (69). Induced moment, in turn, creates a secondary magnetic field superimposed on the external one. Nuclei which are along the axis of the

induced moment in the magnetic field are under stronger magnetic field. The effect is zero at an angle of 54.7° from this axis (magic angle), while nuclei in the plane orthogonal to the principal axis experience a reduction of the magnetic field. The effect of the induced moment decreases with the third power of the distance so only the nearest neighbors are affected by it.

Considerable attention has been paid to the study of SIS resulting from this effect, anisotropic SIS, and as a result some of them can readily be qualitatively identified. The most often seen and also the most analyzed is the effect of the aromatic π-orbital (22,69-72). It induces a shielding on nuclei along the hexagonal axis which decreases both with distance from ring plane and from this axis (71) and a deshielding in the ring plane (69-72). Bonds C-H (73), C-C (70) C-O (70) and C-Cl (74) induce a deshielding along their axis and a shielding at their sides. Reports concerning the intensity of the anisotropic shifts, induced by these bonds, do not, however, agree on the intensities of their effects (70). When an inert compound is dissolved in a series of solvent mixtures containing one nonpolar solvent without pronounced anisotropic effect and an anisotropic solvent, its chemical shift changes linearly with the volume fraction of the anisotropic compound (75). If the specific interaction occurs between the solute and the anisotropic compound the preferential solvation (76) will cause the "excess chemical shift" (75) and the chemical shift for the solute may reach a steady level at certain concentrations below 100% of the anisotropic solvent. Since an agreement

has not been reached about the intensities of the anisotropic SIS, it is not possible, at this time, to separate the contributions of the nonbonding and bonding effects to a total anisotropic SIS. A suggestion has been offered to compare SIS of the polar and nonpolar compounds of similar structure and size (77). Only minimal attention has been paid to the anisotropically induced deviation in Rummens plot for nonpolar solute (51,62). There are no reports of a comparable study for polar solutes.

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C H A P T E R II

OBJECTIVES AND METHODS

Introduction

The commercial importance of poly(2,6-dimethyl-1,4-phenylene oxide)-polystyrene blend has had an impressive growth. So is the number of other empirically-prepared homogeneous polymer blends too. Yet scientific approaches, based solely on the thermodynamic characteristics of compounds have not been sufficient to explain any of the cases of polymer-polymer compatibility (1-3). They have been even less successful in explaining or predicting the more complex cases in which the blend exhibits critical solution temperatures (4-7) or where the blend homogeneity depends on the selection of the solvents for the cosolution of the two polymers (8-10). It is apparent that the mechanism of polymer-polymer compatibility is considerably more complex than has been believed.

The objective of this work is to find an explanation for the compatibility of the polymers beyond the valuable thermodynamic tools. The change in NMR chemical shift as the method for this study has been selected for two main reasons.

NMR techniques have potential for observing the effect of IMI or virtually every atom in an organic compound, thus offering complete information. The new development in the interpretation of the NMR chemical shift by applying Rummens plot allows for a fast and flexible

analysis. This in turn allows for the study of a large number of samples with the possibility for testing the hypotheses by obtaining confirmative or complementary information.

Selection of the Model Systems

One of the polymer blends which is particularly interesting because of the complexity of its properties, is the blend of poly(vinyl methyl ether), PVME and polystyrene, PS (5-10). The homogeneity of this blend when it is prepared from co-solution is solvent-dependent. It was reported that homogeneous blends have been obtained by drying co-solutions in benzene, toluene, p-xylene and tetrachloroethylene while inhomogeneous blends have been obtained from co-solution in chloroform, dichloromethane and trichloroethylene (8-10). Homogeneous blends have an upper and a lower critical solution temperature (5-7). An explanation of such properties, in terms of IMI has not yet been suggested. The blend of poly(2,6-dimethyl-1,4-phenylene oxide), (polyphenyleneoxide, PPO) and PS has been studied in great detail (11-14). The interaction between the aromatic rings in the two polymers has been suggested as the IMI leading to this compatibility (13). Since this conclusion has been reached based on the analysis of the changes in IR and UV spectra it offers an opportunity to compare the results of the NMR spectral analysis with those obtained by other methods.

In order to understand the compatibilities of the fore-mentioned polymer blends it is necessary to observe, in Rummens plot, changes in

spectra of PVME, PS and PPO. Since PS and PPO are not soluble in n-alkanes their oligomers have been analysed. The same kind of analysis as on the compounds of high molecular weight has been performed also on their monomeric models, isopropyl methyl ether, cumene and 2,6-dimethyl phenol. In order to understand better the mechanism of the specific interactions, analysis is performed also on the functional analogues as diethyl ether, ethylene-glycol dimethyl ether, benzene, mesitylene and m-xylene.

The role of the solvent in the formation of the compatibile blend of PVME and PS is elucidated by analysing the IMI of chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene. In order to understand the solubility of poly(vinyl chloride) in cyclic ethers an analysis of SIS is made for 2,4-dichloropentane, 2-chloropropane and 2-chloro-2-methyl propane.

Experimental Procedures

The PVME of two molecular weights have been used. The sample of high molecular weight PVME, PVME(HMW), (GAF, New York) has a reported viscosity average molecular weight M_v of 235,000. Gel permeation chromatography in THF at 25°C indicates a weight average molecular weight, M_w, calculated as if the polymer were PS, of 139,200 and a number average molecular weight, M_n, of 14,800, i.e. an M_w/M_n of 9.4. The PVME sample of low molecular weight PVME(LMW) (Polysciences, Inc., Warrington, Pennsylvania) shows by gel permeation chromatography under the same conditions, M_w = 14,000 and M_n = 2,000, i.e. a M_w/M_n = 7.0.

The oligomeric sample of PS (Pressure Chemicals, Pittsburgh, Pennsylvania) has a narrow distribution of molecular weights, with $\overline{M}_W$ = 600. Oligomeric sample for PPO was a trimer, synthesized and supplied by Dr. D.M. White, General Electric Co., Schenectedy, New York (sample number 10149-70-4).

Isopropyl methyl ether, IPME, was synthesized from isopropyl alcohol and methyl iodide using the Williamson reaction (15). All other compounds used in the study were the purest commercially available grades, used without further purification. When suggested, (16) solvents were kept over freshly-activated molecular sieves, but no further removal of last traces of water has been made. In the first several series of experiments all solvents were flushed with nitrogen before the solution preparation. However, no difference in NMR spectra was observed between freshly-prepared solutions in sealed tubes, solution exposed to air for days and solutions prepared from undeaerated solvents. Subsequently all the test solutions have been prepared without deaeration.

With the exception of the solutions of PVME(HMW) in n-alkanes, all other solutions have been prepared as 3 mol%, i.e. 3 mol % of polymer repeat unit for polymers. Judging from the changes of the chemical shift with concentration reported earlier, (17,18) this concentration should yield a chemical shift undistinguishable from the extrapolated value for the chemical shift at zero concentration. The molar ratio of solvent vs. solute of more than 30:1 insures that the

observed molecule of the solute is engaged in IMI with the solvent molecules only.

Since the solubility of PVME(HMW) in n-alkanes is low, in order to achieve a concentration sufficient for detection by ^{13}C NMR, saturated solutions at 70°C were prepared. These concentrations are considered to be smaller than 3 mol %. In addition all the spectra of the PVME(HMW) were determined at 75° $\pm$ 1°C. Care was taken to avoid polymer precipitation, due to cooling, on transfer to the NMR instrument. An inserted thermostating time of 20 min was employed before taking the spectra.

^{13}C NMR spectra of tetrachloroethylene were recorded at 34 $\pm$ 0.5°C. All other ^{13}C NMR spectra were recorded at 31 $\pm$ 0.5°C. The reason for selecting this temperature instead of standard 25°C was practical; this was the lowest temperature which could be maintained year around.

^{13}C NMR spectra were recorded on a Varian Fourier Transform NMR spectrometer Model CFT-20 (20 MHz). Depending on the solute, different combinations of pulse widths and pulse delays have been applied (Table II-1). Depending on the solute-solvent combination, different minimal number of pulses were averaged for each spectrum. ^{1}H NMR spectra were detemined on a Perkin-Elmer NMR spectrometer Model R12A (60 MHz) at 37°C.

All chemical shifts were determined relative to external standards. For most of the ^{13}C NMR spectra the chemical shifts are

TABLE II-1

Parameters of the NMR Pulse for Different Solutes*

No.	Compound	PW, μs	PD, s
1	PVME(HMW)	7	1
2	PVME(LMW)	7	3
3	PS 17,500	19	2
4	PS 600	19	2
5	PPO	7	1
6	$(PPO)_3$	7	10
7	2,6 DMP	7	1
8	C_6H_6	19	1
9	CUM	7	1.5
10	MES	7	1.5
11	m-XYL	7	1
12	DEE	7	1
13	IPME	7	3
14	EGDME	7	1
15	$CHCl_3$	7	3
16	CCl_4	7	3
17	C_2HCl_3	7	3
18	C_2Cl_4	7	3
19	2,4 DCP	7	3

(*) All symbols as in Appendix, Table A-1.

reported relative to para-dioxane (p-dioxane) in the external standard composed of 10% p-dioxane in D_2O. The exception are spectra for PVME(HMW) which are reported relative to external 10 vol % p-dioxane in DMSO-d_6. This second standard was abandoned since its own DMSO spectrum interferes with the precise determination of the chemical shifts for the weak signals of β-carbons in PVME. Spectra for solutions of PVME(HMW) in n-alkanes were actually determined with external p-dioxane in D_2O and the shifts were recalculated to be expressed as relative to p-dioxane in DMSO-d_6. Most of ^1H NMR spectra have been determined with 10 vol % H_2O in DMSO-d_6 as external standard. Exceptions are spectra for 2,4-dichloropentane which were determined relative to external benzene. All chemical shifts have been corrected for diamagnetic susceptibility using a method previously reported (19). Constants for diamagnetic susceptibility were used as reported (20) without further temperature correction. In cases where experimentally determined values for these constants could not be found, approximate values were found by group-additivity method using values reported by van Krevelen (21).

The identification of spectral peaks has been made according to published ^{13}C and ^1H spectra for the analyzed compounds (22-24). Constants for refractive index (25°C) (20) were used without temperature correction.

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C H A P T E R III

INTERMOLECULAR INTERACTIONS OF CHLOROFORM

Introduction

Chloroform, $CHCl_3$, is one of the most often used general solvents (1). Its molecules are moderately polar (μ = 1.301) in gas phase at 25°C (2)) and it is most polarizable along its threefold axis (3). Negative charge of Cl in $CHCl_3$ is greater than the charge of Cl in CCl_4 (4). In the pure liquid (5-7) or when dissolved in poor solvents (6), molecules of chloroform are self-associating.

Our present interest for intermolecular interactions, IMI, of $CHCl_3$ is induced by its property to prevent the formation of a homogeneous compatible blend from the two otherwise compatible polymers, PVME and PS (8,9). It may be assumed that the influence of the solvent on the compatibility results from the difference in the specific IMI of the two polymers with $CHCl_3$. In order to understand these specific IMI it is our primary interest to analyze the interactions of $CHCl_3$ with alkyl ethers and with aromatic compounds.

In a number of reports (10-16) the solvent-induced changes in chemical shifts, SIS, of the chloroform's NMR spectrum are considered indicators of the specific interaction. The IMI of chloroform have not, however, been analyzed using a Rummens plot to characterize specific interactions.

When $CHCl_3$ is dissolved in a series of n-alkanes both chemical shifts, for its carbon and its proton, change linearly with the Rummens parameter $g^2 = ((n_2^2 - 1)^2/(2n_2^2 + 1))^2$ where n_2 is the refractive index of the solvent (Tables III-1 and III-2 and Figures III-1 and III-2).

The slopes of VDWL for the two nuclei are very different, S_i = 47.37 ppm for proton versus S_i = 81.20 ppm for carbon, i.e., a ratio of 0.58:1. It is noticeable that this ratio is smaller than the ratio between the polarizability of the C-H bond (6.5 $Å^3$) (17) and the average polarizability of $CHCl_3$ molecule (8.53 $Å^3$) (3) which is 0.76:1. It is also smaller than the ratio of the polarizability of $CHCl_3$ along the C-H axis (6.74 $Å^3$) (3) and in the plane orthogonal to this axis (9.31 $Å^3$) (3), which is 0.72:1. It is, however, larger than the ratio of polarizabilities for C-H bond (0.65 $Å^3$) (17) and C-Cl bond (2.8 $Å^3$ (17) or 1.76 $Å^3$) (18) which is 0.23 to 0.37:1.

It may be assumed that the ionization potential of the $CHCl_3$ molecule affects the chemical shifts of both of its nuclei in the same manner. It appears then that the difference between their S_i values reflects chiefly the difference in the polarizabilities of the two distinct structural groups - the C-H bond and the CCl_3 group. However, the S_i values do not seem to be related to the polarizabilities of the C-H and C-Cl bonds. A reduction of about 20% (0.58 vs. 0.72) may probably be attributed to the fact that the chemical shift of the carbon reflects the involvement in the dispersive interaction of both chlorine and the hydrogen.

TABLE III-1

^{13}C NMR Chemical Shifts for Chloroform in Different Solvents*

No.	Solvent	$g^2.10^2$	δcorr	δVDWL	Δδ
1	C5	3.24	8.88		
2	C7	3.63	9.21		
3	C8	3.78	9.33		
4	C10	3.96	9.47		
5	C16	4.26	9.71		
6	C_6H_{12}	4.15	9.49	9.63	-0.14
7	$CHCl_3$	4.43	10.10	9.85	0.85
8	CCl_4	4.62	10.24	10.01	0.23
9	CCl_4	4.62	10.24	10.01	0.23
10	CH_2Cl_2	4.13	10.84	9.61	1.23
11	1,2 DCE	4.43	11.33	9.85	1.48
12	1,1,1 TCE	4.31	10.51	9.76	0.75
13	1,1,2,2 TCE	5.08	11.49	10.38	1.11
14	2CP	3.51	10.20	9.10	1.10
15	TBC	3.60	10.04	9.18	0.86
16	CH_2HCl_3	4.84	10.09	10.19	-0.10
17	C_2Cl_4	5.24	10.15	10.51	-0.36
18	DEE	3.15	10.49	8.81	1.68
19	DEE	3.15	10.49	8.81	1.68
20	IPME	3.24	10.49	8.89	1.60
21	DIPE	3.38	10.64	9.00	1.64
22	DIPE	3.38	10.64	9.00	1.64
23	EGDME	3.52	11.50	9.11	2.45
24	EGDME	3.52	11.57	9.11	2.46
25	P-DIOX	4.09	11.03	9.58	1.45
26	P-DIOX	4.09	11.02	9.58	1.44
27	THF	3.89	11.21	9.42	1.79
28	C_6H_6	5.17	9.82	10.45	-0.63
29	TOL	5.12	9.71	10.42	-0.71
30	CUM	5.05	9.98	10.36	-0.38
31	MES	5.13	10.10	10.42	-0.32

*All values at 31°C relative to external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix Table A-2). Symbols as in Appendix Table A-1.

**Van der Waals line has the correlation 0.9998 for equation

$$\delta = 6.25 + 81.20\ g^2 \text{ (ppm)}$$

TABLE III-2

^{1}H NMR Chemical Shifts for Chloroform in Different Solvents*

No.	Solvent	g^2	δcorr	δVDWL	Δδ
1	C6	3.47	3.01		
2	C7	3.63	3.09		
3	C8	3.78	3.16		
4	C9	3.89	3.21		
5	C10	3.96	3.26		
6	C16	4.26	3.38	**	
7		3.52	3.12	3.04	0.08
8	C_6H_{12}	4.15	3.28	3.34	-0.06
9	$CHCl_3$	4.43	4.00	3.47	0.53
10	CCl_4	4.62	3.91	3.56	0.35
11	C_2HCl_3	4.84	3.55	3.67	-0.12
12	C_2Cl_4	5.24	3.67	3.85	-0.18
13	DEE	3.15	3.65	2.86	0.79
14	IPME	3.24	3.60	2.91	0.69
15	DIPE	3.38	3.62	2.97	0.65
16	EGDME	3.52	3.89	3.04	0.85
17	P-DIOX	4.09	3.96	3.31	0.65
18	THF	3.89	4.02	3.22	0.80
19	C1OH	2.84	3.65	2.72	0.93
20	ECL	4.66	4.28	3.58	0.70
21	C_6H_6	5.17	2.00	3.82	-1.82
22	TOL	5.12	2.00	3.80	-1.80
23	CUM	5.05	2.19	3.76	-1.57
24	MES	5.13	3.03	3.80	-0.77

*All values at 37 ± 0.5°C relative to external standard (10 vol% H_2O in $DMSOd_6$) corrected for diamagnetic susceptibility (see Appendix Table A-3). Symbols as in Appendix Table A-1.

**Van der Waals line has the correlation 0.9982 for the equation

$$\delta = 1.37 + 47.37\ g^2\ (ppm)$$

Fig. III-1. Rummens plot for ^{13}C NMR chemical shifts of chloroform in different solvents.

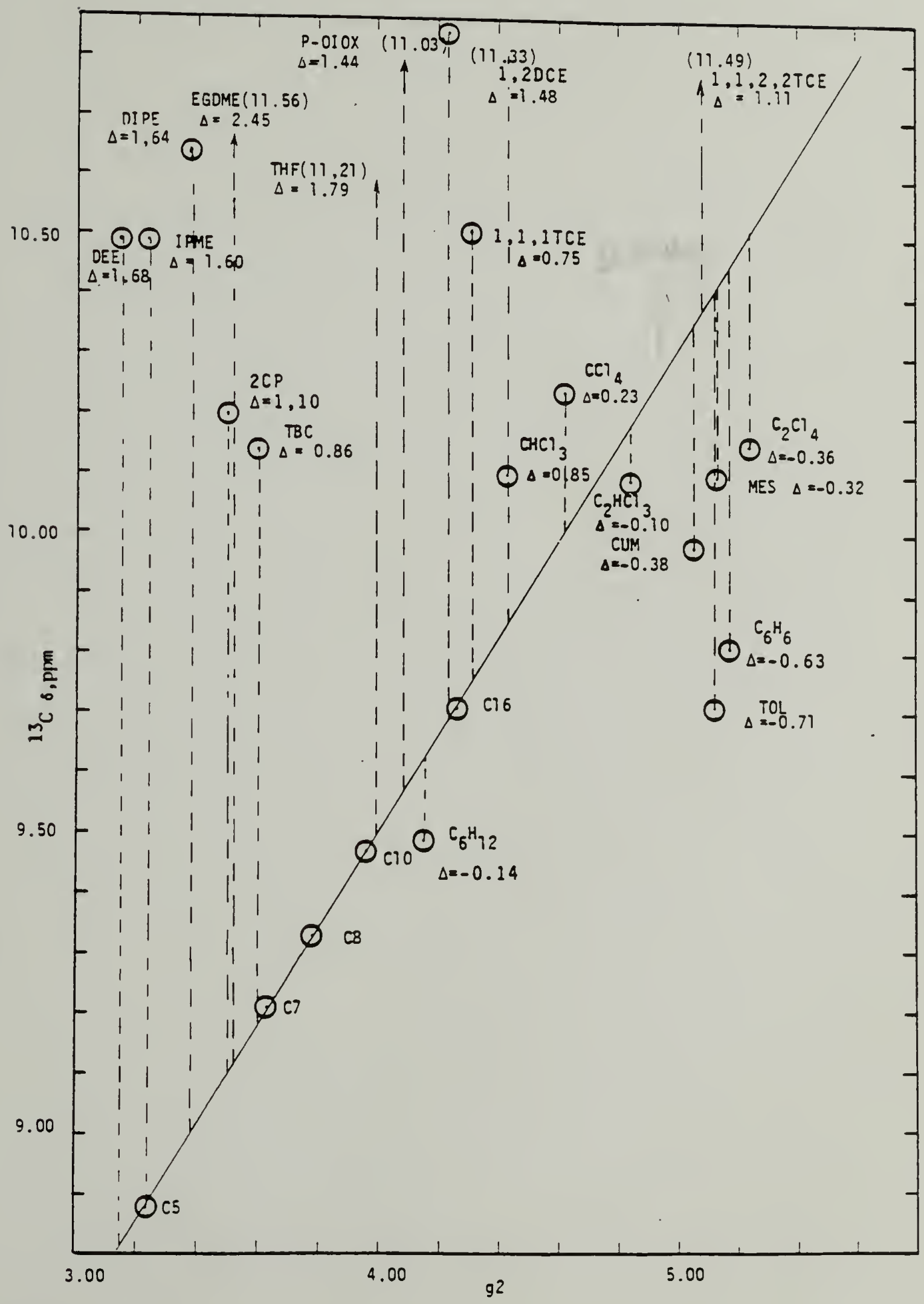
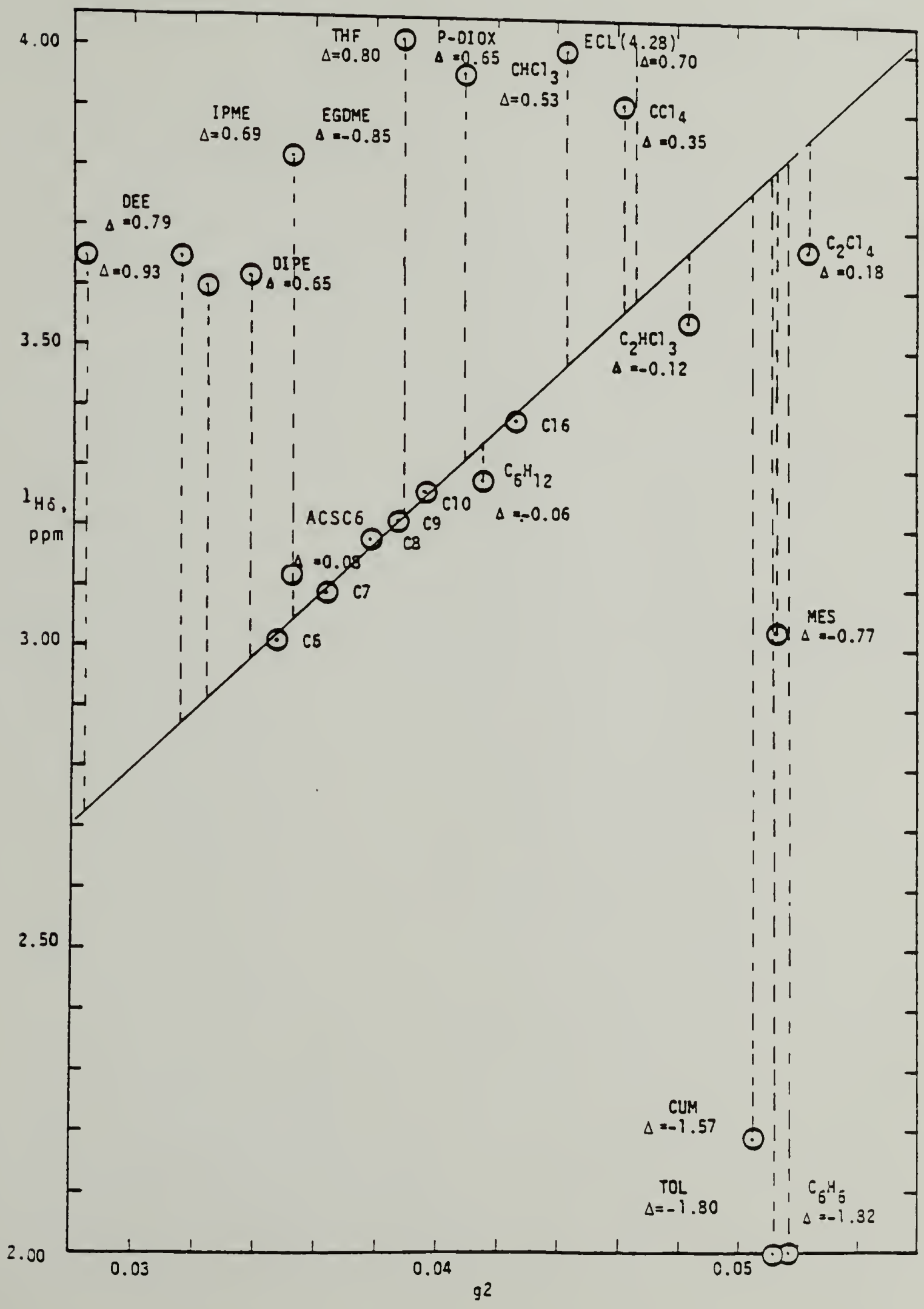

P-OIOX
Δ=1.44
(11.03)
(11.33)
1,2DCE
Δ =1.48
(11.49)
1,1,2,2TCE
Δ = 1.11
EGDME(11.56)
Δ= 2.45
DIPE
Δ=1,64
THF(11,21)
Δ = 1.79
10.50
DEE
Δ=1,68
IPME
Δ = 1.60
1,1,1TCE
Δ=0.75
2CP
Δ=1,10
TBC
Δ = 0.86
CCl4
Δ=0.23
CHCl3
Δ =0.85
C2Cl4
Δ=-0.36
MES Δ =-0.32
C2HCl3
Δ =-0.10
CUM
Δ=-0.38
10.00
C6H6
Δ=-0.63
C16
TOL
Δ =-0.71
13C δ,ppm
9.50
C6H12
Δ=-0.14
C10
C8
C7
9.00
C5
3.00
4.00
5.00
g2

Fig. III-2. Rummens plot for ^{1}H NMR chemical shifts of chloroform in different solvents.


4.00
3.50
3.00
2.50
2.00
$^1H\delta$, ppm
0.03
0.04
0.05
g2
THF
Δ=0.80
P-DIOX
Δ =0.65
CHCl3
Δ=0.53
ECL(4.28)
Δ=0.70
CCl4
Δ =0.35
IPME
Δ=0.69
EGDME
Δ =-0.85
DEE
Δ =0.79
Δ =0.93
DIPE
Δ =0.65
C2Cl4
Δ =0.18
C2HCl3
Δ =-0.12
C16
C6H12
Δ =-0.06
C10
C9
C8
ACSC6
Δ =0.08
C7
C6
MES
Δ =-0.77
CUM
Δ =-1.57
TOL
Δ=-1.80
C6H6
Δ =-1.82

$CHCl_3$ dissolved in cyclohexane shows in ^1H NMR only a negligible upfield deviation from VDWL (-0.06 ppm). A little stronger upfield deviation (-0.16 ppm) appearing in ^{13}C NMR indicated that several molecules of C_6H_{12} cause the anisotropic effect on the molecule of $CHCl_3$ (19). The intensity of deviations corresponds to the reported effects of C_6H_{12} on other nonpolar (20) and polar molecules (21) and does not suggest any interaction stronger than dispersive.

Interactions with Polar Compounds

Since $CHCl_3$ is a polar compound, it may be assumed that it can enter in dipole-dipole interactions with other polar compounds. Some authors (5,6) assume that IMI in the pure $CHCl_3$ is dipolar in its nature. Deviations from VDWL have been determined in both ^{13}C and ^1H NMR for $CHCl_3$ dissolved in a number of polar compounds (Tables III-1 and III-2). Those deviations do not show any correlation with the Tiffon-Dubois parameter $\mu_2/(V_1^{1/3} + V_2^{1/3})^{-3}$ (21) (see Chapter I, Equation I-8), neither could they be correlated with values for dipolar moments of those compounds. This suggests that, at least with polar solvents applied in this analysis, $CHCl_3$ does not form any purely or predominantly coulombic interaction.

Most commonly $CHCl_3$ is considered to interact with another polar compound through a hydrogen bond in which it is a proton donor (11-15, 22-27). There are reports, however, that it may interact also through charge-transfer complex engaging its chlorine (28-34). The intensity of this charge-transfer interaction is, however, considered to be

small, particularly in the case of oxygen as second participant in the complex (29-34).

In our experiments deviations of chloroform chemical shifts from VDWL induced by several solvents indicate deshielding of both hydrogen and carbon. When ^{13}C deviations in those solvents are plotted as a function of their ^{1}H analogues (11) (Figure III-3) a noticeably linear trend is seen in the change of the deviations. Such a trend is reported earlier (11) and attributed to the hydrogen bonding between $CHCl_3$ and solvents. For all 10 points the correlation is 0.961 and the average deviation from the correlation line is $\pm$ 0.11 ppm. The correlation is, however, much better (0.995) for a series containing CCl_4, $CHCl_3$, p-dioxane, isopropyl methyl ether, IPME, and ethyleneglycol dimethyl ether, EGDME. The unexpected finding in this experiment is that CCl_4 appears as a proton acceptor, forming a hydrogen bond with $CHCl_3$. This problem will be addressed later.

If only the hydrogen were involved in the hydrogen bond, based on previously published theoretical work (35,36), it may be expected that its deviation from VDWL would be stronger than that of the carbon. This is indeed the case when $CHCl_3$ is dissolved in CCl_4. For all other solvents applied in this analysis the opposite is true. Stronger deviation for carbon suggests that the same molecule of $CHCl_3$ may simultaneously be both a proton donor and a proton acceptor.

For pure $CHCl_3$ it may then be concluded that its cohesive interaction consists of the hydrogen bonding between the molecules acting both as electron donors and as proton donors. It has already been

reported that pure $CHCl_3$ has a tendency toward association (6,12,37,38). The degree of association was, however, found to be only an incomplete dimerization (7). The results reported here suggest that this association may have a form of either clusters or associated chains. If our assumption was correct, both the density and the viscosity of $CHCl_3$ should be affected by the temperature considerably more than a compound without similar bonding properties such as CCl_4. At this time we are not aware of any work dealing with either the densities or viscosities of liquids which may support or disprove of our speculation.

Interactions with Carbon Tetrachloride

The interaction of $CHCl_3$ with CCl_4 was reported to be weaker than the interaction with $CHCl_3$ itself (37) but stronger than that with a van der Waals solvent, C_6H_{12} (38,39). Since the $-CCl_3$ group in $CHCl_3$ has a net change (4,40) CCl_4 cannot approach $CHCl_3$ from the side of $-CCl_3$ group. A further implication is that the interaction between the two compounds may not be a dispersive interaction in which $CHCl_3$ interact with CCl_4 at random. The $CHCl_3$ dissolved in CCl_4 shows a deshielding of 0.35 ppm for its hydrogen and 0.23 ppm for the carbon. As mentioned before, this suggests that the two compounds interact through the hydrogen of the $CHCl_3$. This is, however, not a sufficient proof that this is the exact mode of the IMI.

The assumption that CCl_4 forms a hydrogen bond with $CHCl_3$ has never been stated before. Here it is made based on three indicators:

a) the deshielding of both compounds involved,

b) when $CHCl_3$ is dissolved in CCl_4 its hydrogen is more deshielded than the carbon, and

c) in $\Delta\ ^{13}C$ vs. $\Delta\ ^{1}H$ plot for $CHCl_3$ dissolved in different solvents CCl_4 has the position on the same line with other compounds which are known to form hydrogen bonds. The only nondispersive mode of the interaction which has been suggested before, for the two compounds, was a dipole ($CHCl_3$)-induced dipole (CCl_4) interaction (41). This suggestion has been made speculatively to explain the increase of the optical density of the $CHCl_3$ - CCl_4 mixture with an increase of $CHCl_3$ concentration.

It is interesting to note that the deviation for $CHCl_3$ carbon in CCl_4 (0.23 ppm) is very near to the deshielding of 0.27 ppm for the carbon of CCl_4 dissolved in $CHCl_3$ (see Chapter IV, Table IV-1). The exact meaning of this similarity in deshielding intensities for both of the interacting compounds is not yet understood. The intensities of the deviations from VDWL, suggest, however, that the interaction between the two compounds must be weak. This is in agreement with the finding that ^{1}H nuclear spin-lattice relaxation time, T_1, for $CHCl_3$ dissolved in CCl_4 does not change with the concentration (42).

Interactions with Ethers

Interactions of $CHCl_3$ with ethers have been studied using calorimetry (22,24,34,43-50), ebuliometry (44), volumetry (51-53), gas-liquid chromatography (31), changes in dielectric properties (54),

dipole moment (30), Kerr constant (33) and glass transition temperature (55). It was also studied by light scattering (56) and by observing changes in Raman (27), IR (22,23,57,58) and NMR spectra (10,12-15,28,29,32,57).

The interaction between the $CHCl_3$ and ethers (often referred to, summarily, as chloroform-ether complex (13,54,56) is most often characterized as a hydrogen bond between hydrogen in $CHCl_3$ and the oxygen in the ether (10,12,14,15,22,27,28,33,55) forming 1:1 complexes (46,56,59). The dielectric behavior of the mixture indicates the possibility that a complex of 2 $CHCl_3$ with 1 molecule of diethyl ether, DEE, may be formed (54). It was found that the interaction is different with ethers which have more than one n-electron donor site (14) or if the n-donor site is sterically hindered (23). More recently, the interaction between $CHCl_3$ and ether has been considered as a combination of the H-bonding and charge-transfer complexing between the chlorine in $CHCl_3$ and oxygen in ether (23, 28-32). It was concluded, however that due to low charge-acceptor strength of Cl and low charge-donor strength of oxygen this mode of interaction does not play a significant role in the overall interaction (29-32). More attention has been paid lately to the possibility that $CHCl_3$ can also interact with electron deficient ends of ether's molecule as electron donor (29,59).

Our experimental results indicate a deshielding of both proton and carbon when $CHCl_3$ is dissolved in alkyl or cycloalkyl ethers (Tables III-1 and III-2). Intensities of the deviations, both for carbon and

proton, suggests that the IMI between $CHCl_3$ and ethers is stronger than the cohesive IMI of $CHCl_3$. Linear correlation between the ^{13}C and ^{1}H deviations (see Figure III-3) is in an agreement with the concept of hydrogen bond interaction. As mentioned before the 2.5:1 difference in the intensities for ^{13}C and ^{1}H deviations suggest that CCl_3 group does play a role in the interaction with ethers.

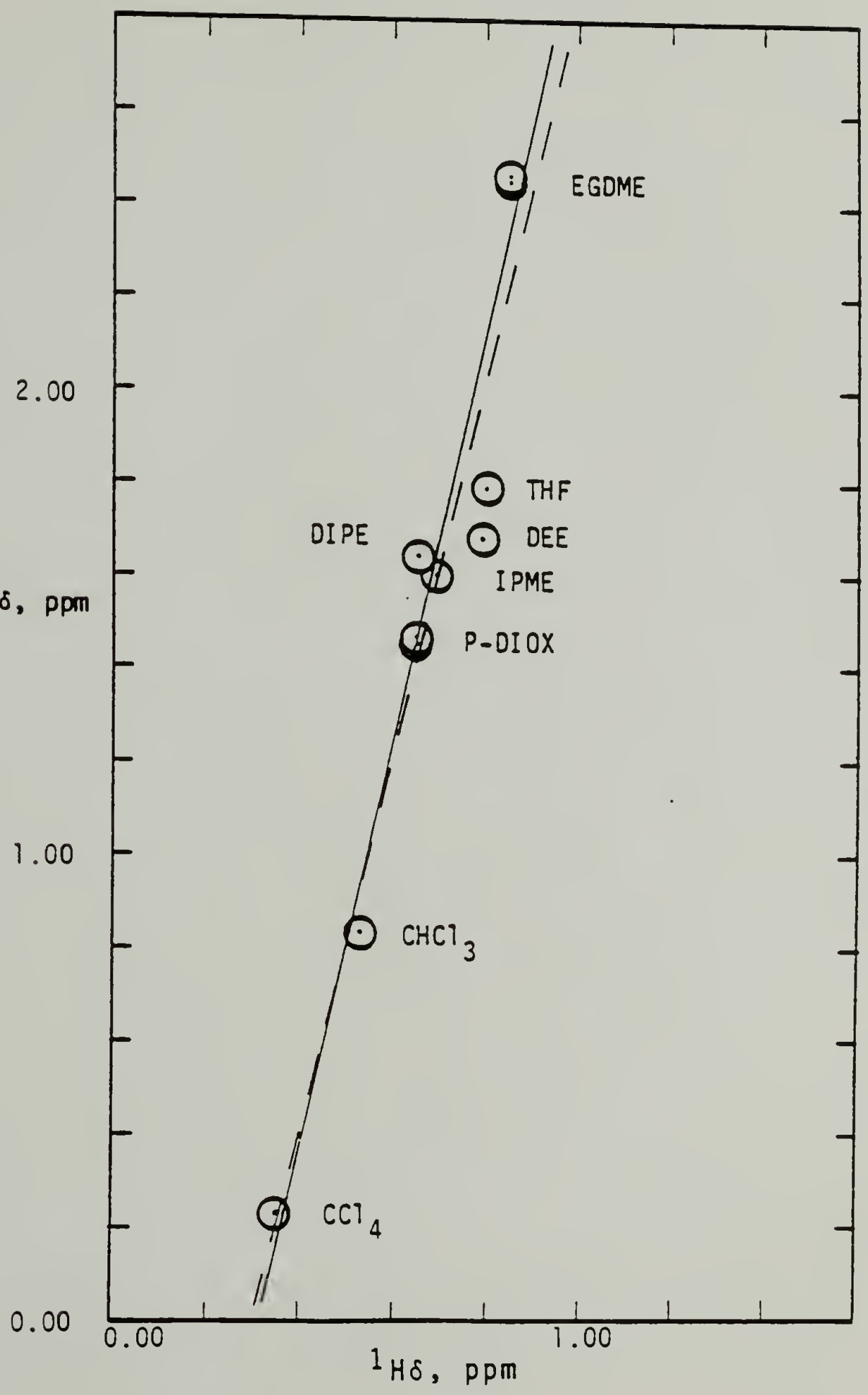
DEE, IPME and EGDME dissolved in $CHCl_3$ show deshieldings of all their carbons (Chapter VII, Tables VII-1 to VII-3 and Table III-3). In DEE and IPME, deshielding is stronger for the more electron deficient α and methoxy carbons. The intensity of the deshielding rules out any possibility that its origin may be an anisotropic effect of the C-Cl bond of $CHCl_3$ attached to the oxygen. In the case of EGDME, the deshielding is much smaller (≃ 1/3) for α carbons, which may be explained by the steric unaccessibility of both those sites to separate chloroform molecules. At the same time, the exposed methoxy carbon in EDGME shows a strong deshielding. Since it was demonstrated that $CHCl_3$ does not form dipole-dipole interactions it may be concluded that $CHCl_3$ interacts with ethers in two ways simultaneously. It acts as proton donor toward the oxygen and as electron donor with electron deficient alkyl segments. This is in agreement with already mentioned earlier findings (29,59), but does not agree with the findings of Taft and coworkers (60) that neither aliphatic nor cycloaliphatic ethers can form hydrogen bonds as proton donors. Additional study, applying NMR relaxation measurements or IR spectroscopy is necessary to clarify this contradiction.

TABLE III-3

Chloroform-Induced Deviations from VDWL for Some Alkyl Ethers and Aromatic Compounds

Compound	Carbon	$^{13}C\Delta$	$^{1}H\Delta$
DEE	α	+0.73	
DEE	β	+0.48	
IPME	$-OCH_3$	+0.92	
IPME	α	+0.88	
IPME	β	+0.51	
EGDME	$-OCH_3$	+1.06	
EGDME	α	+0.29	
Benzene	-	+0.70	+0.47
Cumene	Ci	+1.16	
	Co	+0.69	
	Cm	+0.85	
	Cp	+0.64	
	average	+0.74	+0.73
Mesitylene	Ci	+1.40	
	Co	+0.55	+0.55
	$-CH_3$	+0.55	+0.45

Fig. III-3. Correlation between ^{13}C and ^{1}H chemical shifts of chloroform dissolved in deshielding-inducing polar solvents.


EGDME
THF
DIPE
DEE
IPME
P-DIOX
CHCl3
CCl4
2.00
1.00
0.00
0.00
1.00
13Cδ, ppm
1Hδ, ppm

Deviation of ^{1}H shift from VDWL induced by DEE are 15% stronger than the one induced by diisopropyl ether, DIPE. This corresponds rather closely to 12% difference in the reported heats of mixing of $CHCl_3$ with the two ethers (43). The difference between the corresponding ^{13}C deviations is, however, almost negligible, 2.5%. Intensities of both proton and carbon deviations changes in order THF > DEE > p-dioxane. This disagrees, however, with the findings of Weikowisch (57) that intensities of the interactions decreases in the order DEE > p-dioxane > THF.

Interactions with Aromatic Compounds

The existence of the interaction between $CHCl_3$ and aromatic compounds has been determined calorimetrically (22,61,62) from the molar polarization of $CHCl_3$ (63), from the Kerr constant (33,64,65) and from the changes in UV (66), IR (30,67,68), and Raman (67,69) spectra. In NMR spectra this interaction has been recorded from the change in chemical shifts (10,11,16,70), nuclear relaxation times (42) and nuclear Overhauser effect, NOE, (71). Although different modes of the interaction have been discussed (10,11,70) this interaction is usually considered a π-hydrogen bond between the electron-poor hydrogen and the π orbital in the aromatic compound (61-64,66,68). The fact that excess enthalpy of mixing is more negative for alkyl substituted aromatics than for benzene (61,63) apparently confirms this conclusion. Similarly, the UV spectra show a higher intensity of the interaction with mesitylene and xylenes than with benzene (66). A dipole ($CHCl_3$)-

induced dipole (benzene) interaction was also suggested as the possible mode of interaction between the two compounds (70).

Most authors have assumed a 1:1 complex (72,73) but its existence has been disputed based on NOE data (71). Ratios of 1 C_6H_6:2 $CHCl_3$ (66) and 2 C_6H_6:1 $CHCl_3$ (67) have also been suggested, as is the solvatation of $CHCl_3$ with several, up to 12, molecules of benzene (16).

From the changes of the line intensities in Raman spectra it was concluded that the interaction of $CHCl_3$ with benzene is stronger than the interaction between molecules of $CHCl_3$ (69). Spin-lattice nuclear relaxation time, T_1, for hydrogen in $CHCl_3$ does not, however, change with the concentration in benzene (41). This may suggest that the energy of interaction between $CHCl_3$ and benzene may be at the same level of the interaction energy between the molecules of $CHCl_3$.

Our experimental results indicate a strong shielding of the hydrogen and a moderate shielding of carbon in $CHCl_3$ dissolved in aromatic solvents (see Tables III-1 and III-2 and Figures III-1 and III-2).

Aromatic molecules dissolved in $CHCl_3$ show deshielding of all nuclei (Chapter VI, Tables VI-1 to VI-8 and Table IV-3). Average deshielding for unsubstituted carbons in cumene is 0.74 ppm, very near to the 0.73 ppm for deviation of its hydrogens and to the deviation of 0.70 for carbons in benzene. The most noticeable change in the spectra is the strong deshielding of the substituted carbons in mesitylene and cumene (1.16 and 1.40 ppm, respectively). Since the deshielding of any other ring carbon and the deshielding of the methylcarbon in mesitylene are considerably smaller, those deviations

cannot be considered "transmitted-through-bond" effects. They may be attributed only to the changes in the character of the π-orbital. At present, we do not as yet understand the exact character of this change. It appears significant enough, however, that such change in shielding occurs when an aromatic molecule is engaged in the interactions with a hydrogen donor as $CHCl_3$. To the best of our knowledge, there is no theoretical considerations suggesting any such change either in the character of π-orbital nor in the shielding of the substituted carbon.

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C H A P T E R IV

INTERMOLECULAR INTERACTIONS OF CARBON TETRACHLORIDE

Introduction

The molecule of the octapolar (1) tetrachloromethane, (carbon tetrachloride, CCl_4),is usually considered, for practical purposes, to be a nonpolar, spherical (2) and free rotating molecule. As other such compounds, it is most often believed to be a nonpolar solvent forming only weak van der Waals interactions (3-5). A number of reports, however, have suggested evidence that this is an over-simplification which hinders the full understanding of the properties of this solvent (2,5-9).

CCl_4 is a solvent for a number of polymers (10), so the study of the mechanisms of its IMI is a matter of general interest. Our specific interest in the IMI of CCl_4 was initiated by the influence it has on the homogeneity of the blend of poly(vinyl methyl ether), PVME, with polystyrene, PS. Drying the cosolution of these two polymers in CCl_4 yields a nonhomogeneous, opaque blend which after resting approximately 30 days at room temperature became transparent. This behavior of the blend indicates that CCl_4 has some specific, but weak intermolecular interaction with one, or with both, of the two polymers. There are, however, no reports in the literature concerning any such interaction. In order to gain understanding of the mechanism leading to the interactions with the two polymers our aim is to understand first the mechanisms of the IMI of CCl_4 with ethers and

aromatic compounds of low molecular weight. To this goal, the change of the chemical shifts for CCl_4 in the Rummens plot will be compared with the earlier reported findings about the IMI of CCl_4 with other compounds.

The ^{13}C NMR chemical shifts of CCl_4 dissolved in a series of n-alkanes at 31°C (Table IV-1 and Figure IV-1) show a linear dependence on the Rummens parameter g^2. This is in agreement with the reported very small excess enthalpies of mixing (11-13) and with the expected van der Waals interactions. Deviation from VDWL induced by cyclohexane (-0.03) corresponds to the anisotropic deviations induced on nonpolar solutes (14) and indicates the absence of any specific interaction. This is in agreement with the reported weakly endothermic mixing of CCl_4 and C_6H_{12} (15) and values of the Kerr constants of their mixture (16).

Neutron scattering of pure, liquid CCl_4 (6-8) indicates that its molecules have a preferred mutual position which contradicts the usual conception of the freely rotating spherical molecule (2). In it the carbon of one molecule approaches the chlorine of the other along its C-Cl axis (7). In this configuration the anisotropic effect of C-Cl bonds (17) may be expected to cause a small shielding. The pure CCl_4 indeed shows a small (0.08 ppm) deshielding. This small downfield shift may represent a combination of the interaction-induced deshielding and the anisotropic shielding. This conclusion contradicts the findings based on the magneto-optic rotation of pure CCl_4 which does not indicate any specific interaction (18). Apparently this subject needs further study.

TABLE IV-1

^{13}C NMR Chemical Shifts for Carbon Tetrachloride in Different Solvents[a]

No.	Solvent	g^2	δcorr	δVDW	Δδ
1	C5	3.24	28.58[b]		
2	C7	3.63	28.80[b]		
3	C7	3.63	28.81[b]		
4	C9	3.87	28.96[b]		
5	C11	4.04	29.07[b]		
6	C16	4.26	29.19[b]		
7	C_6H_{12}	4.15	29.10	29.13	-0.03
8	$CHCl_3$	4.43	29.57	29.30	0.27
9	CCl_4	4.62	29.49	29.41	0.08
10	CCl_4	4.62	29.48	29.41	0.07
11	C_2HCl_3	5.24	29.57	29.79	-0.22
12	DEE	3.15	28.45[c]	28.52	-0.07
13	DnPrE	3.55	28.70[c]	28.76	-0.063
14	DnBE	3.79	28.85[c]	28.99	-0.059
15	DnPeE	3.97	28.98[c]	29.018	-0.038
16	DnHE	4.08	29.05[c]	29.085	-0.035
17	IPME	3.24	28.48	28.575	-0.095
18	IPME	3.24	28.48	28.575	-0.095
19	DIPE	3.38	28.51	28.660	-0.15
20	DIPE	3.38	28.53	28.660	-0.13
21	p-DIOX	4.09	29.16	29.09	0.07
22	p-DIOX	4.09	29.16	29.09	0.07
23	p-DIOX	4.09	29.15	29.09	0.06
24	THF	3.89	29.09	28.97	0.12
25	EGDME	3.52	28.79	28.74	0.05
26	EGDME	3.52	28.77	28.74	0.03
27	C1OH	2.85	28.50	28.338	0.165
28	C2OH	3.26	28.70[d]	28.587	0.113
29	C3OH	3.59	28.87[d]	28.787	0.083
30	C4OH	3.77	29.00	28.897	0.103
31	C5OH	3.93	29.05[d]	28.994	0.056
32	C8OH	4.21	29.19[d]	29.164	0.026
33	C12OH	4.39	29.27[d]	29.773	0.003

[a]All values at 31 ± 0.5°C relative to the external standard, (10 vol % p-dioxane in DMSOd6), corrected for diamagnetic susceptibility (see Appendix, Table A-3). Symbols as in Appendix, Table A-1.

[b] Van der Waals line has the correlation 0.9994 for the equation

$$\delta = 60.70\ g^2 + 26.608$$

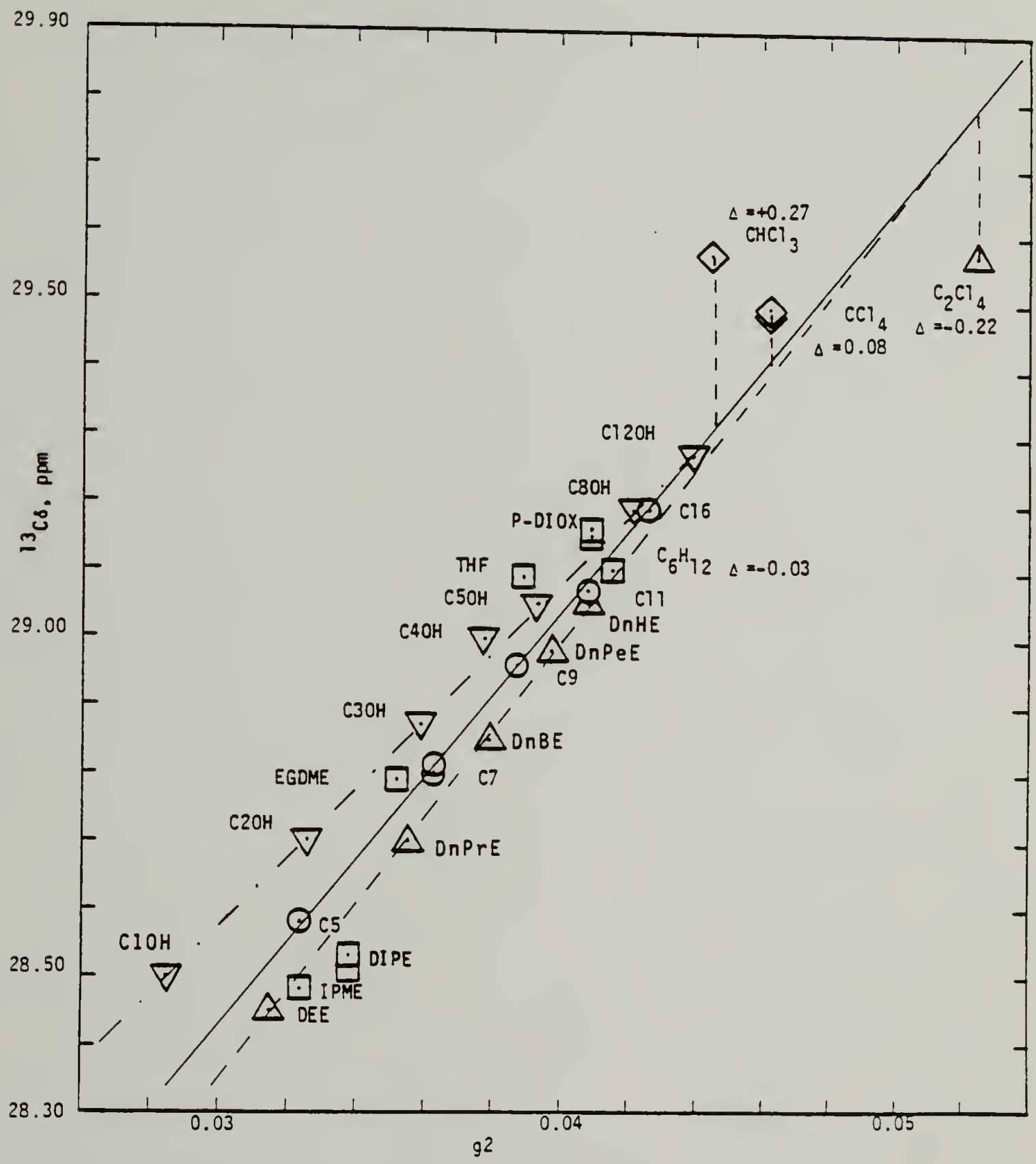
[c]Chemical shifts for symmetrical di-n-alkyl ethers change linearly with g^2 with the correlation 0.9997 for the equation

$$\delta = 64.60\ g^2 + 26.41 \text{ (ppm)}$$

[d]Chemical shifts for linear 1-hydroxy alcohols change linearly with g^2 with the correlation 0.9998 for the equation

$$\delta = 50.43\ g^2 + 27.06 \text{ (ppm)}$$

Fig. IV-1. Rummens plot for ^{13}C NMR chemical shifts of carbon tetrachloride in different solvents.


29.90
29.50
29.00
28.50
28.30
$^{13}C\delta$, ppm
0.03
0.04
0.05
g2
Δ =+0.27
CHCl3
CCl4
Δ =0.08
C2Cl4
Δ =-0.22
C12OH
C8OH
C16
P-DIOX
C6H12
Δ =-0.03
THF
C5OH
C11
DnHE
C4OH
DnPeE
C9
C3OH
DnBE
EGDME
C7
C2OH
DnPrE
C5
C1OH
DIPE
IPME
DEE

Interactions with Aromatic Compounds

Interactions between CCl_4 and benzene have attracted considerable attention. Results from several different kinds of experiments indicate that a specific interaction exists between the two compounds. At low temperatures a solid complex is formed (15). The excess enthalpy (15,19-23) and excess volume of mixing (19,20,24,25) increase with the temperature. Additional indications come from measuring heat capacity (26), optical anisotropy (18), magneto-optical rotation (28) and the Kerr constant (16) and from UV (19) and Raman spectra (27).

The character of the interaction is most often considered to be a charge transfer complex between the π-orbital of the aromatic compound as π-electron donor and the empty 3d orbital of chlorine in CCl_4 as electron acceptor (19,24-32). Enthalpies of formation of those complexes have been reported to be 1.3 (33) or 3.5 kcal/mole (34). This subject has been reviewed in detail (31,35). In addition, a suggestion has been made that a quadripole (benzene)-induced dipole (CCl_4) interaction may take place between the two compounds (18).

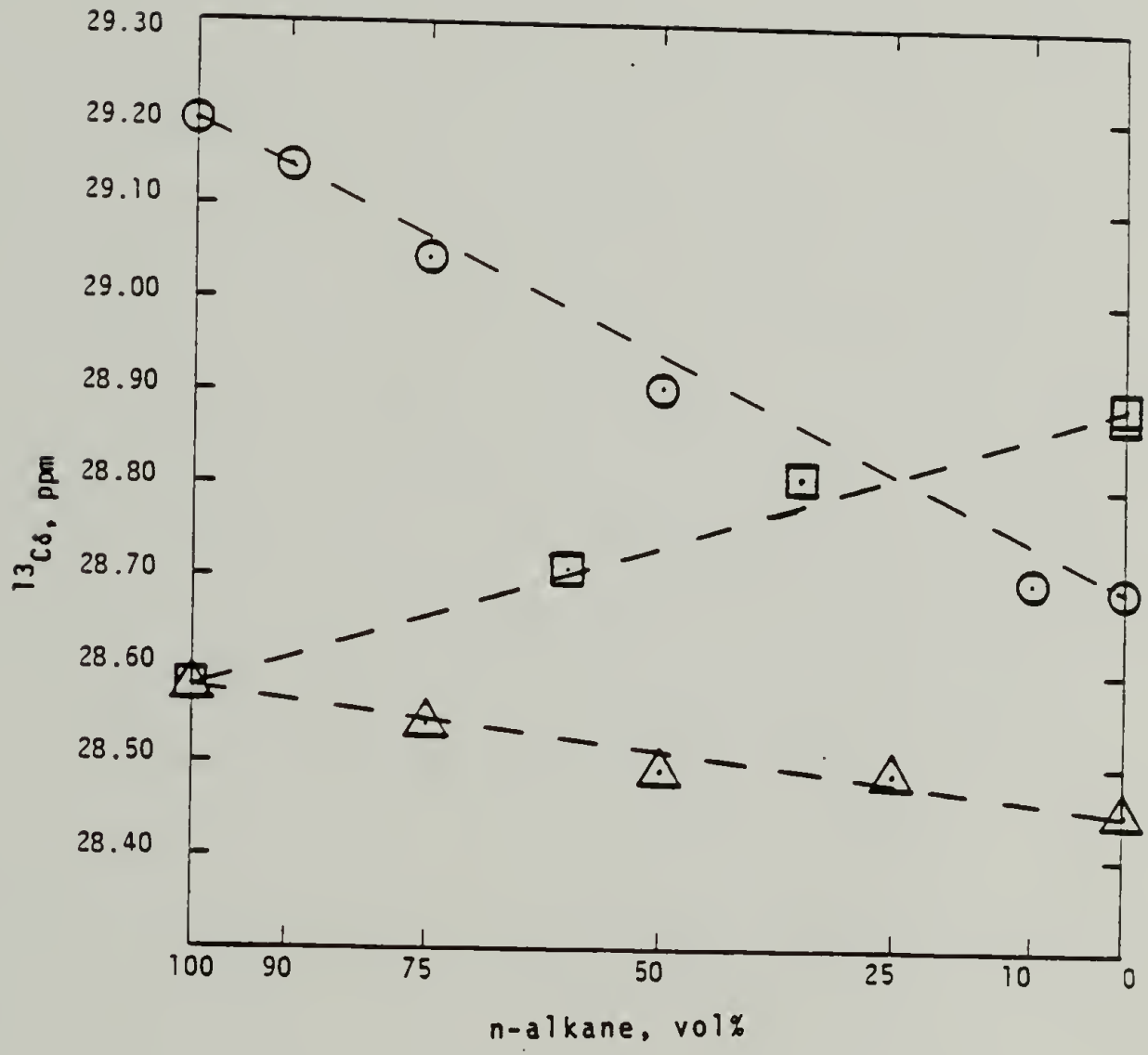
CCl_4 dissolved in benzene shows, in the Rummens plot, a large deviation upfield (-1.04 ppm) characteristic for the anisotropic effect of a π orbital (4,14). In a series of n-hexadecane-benzene mixtures the chemical shift for CCl_4 shows a very small excess chemical shift (36) upfield from the volume-averaged values (see Table V-2 and Figure V-2). Although this excess shift (-0.05 ppm at 90% C_6H_6) is larger than the standard error of the experiment (± 0.02 ppm) its

TABLE IV-2

Chemical Shifts of CCl_4 in Binary Mixtures

No.	Comp #1	Vol %	Comp #2	Vol %	Δδ	δ	δcorr
1	C16	100	C_6H_6	0	-0.157	29.35	29.19
2	"	90	"	10	-0.160	29.30	19.14
3	"	75	"	25	-0.165	29.21	29.045
4	"	50	"	50	-0.174	29.08	29.905
5	"	10	"	90	-0.187	29.89	29.7,0
6	"	0	"	100	-0.191	28.88	28.69
7	C5	100	DEE	0	-0.36	28.94	28.58
8	"	75	"	25	-0.36	28.90	28.54
9	"	50	"	50	-0.36	28.85	28.49
10	"	50	"	50	-0.36	28.85	28.49
11	"	25	"	75	-0.36	28.85	28.49
12	"	0	"	100	-0.36	28.81	28.45
13	"	100	C30H	0	-0.35	28.94	28.58
14	"	60	"	40	-0.31	29.02	28.71
15	"	35	"	65	-0.28	29.09	28.81
16	"	0	"	100	-0.24	29.11	28.87
17	"	0	"	100	-0.24	29.13	28.89

Fig. IV-2. The ^{13}C NMR chemical shifts of carbon tetrachloride in mixtures of n-alkanes and other solvents: (○) n-hexadecane and benzene (□) n-pentane and n-propyl alcohol; (△) n-pentane and diethyl ether.


29.30
29.20
29.10
29.00
28.90
28.80
28.70
28.60
28.50
28.40
$^{13}C\delta$, ppm
100
90
75
50
25
10
0
n-alkane, vol%

size, relative to the total anisotropic shift, is too small to be considered a definite indicator of the preferential solvation and of an interaction considerably stronger than van der Waals.

This absence of the strong indicators for the specific interaction in a n-hexadecane-benzene mixtures at 31°C may eventually be attributed to the properties this mixture has at this particular temperature. At 30°C the mixing of benzene and CCl_4 has been reported to be almost ideal (20). It is weakly endothermic (28.1 cal/mol at 48 vol % CCl_4 (20) and its excess value is very low (+0.009 ml/mole at 48 vol % CCl_4 (20)).

The aromatic compounds dissolved in CCl_4 all show deshieldings for all carbons and protons at the ring (see Chapter VI, Tables VI-1 to VI-4 and the Table IV-3). The deshielding of the unsubstituted carbons apparently decreases as the possibility for steric hindrance by the substituent rises. However it is interesting to note that the average deviation for ring carbons of cumene is similar to that of benzene (0.35 vs. 0.33). All substituted carbons show deshielding too. This is the pattern reminding of the aromatics dissolved in chloroform (Table III-3). However for both unsubstituted and substituted carbons the intensity of the deshielding is only a fraction of that induced by $CHCl_3$. The deshielding of the substituted carbons and the more intensive deshielding of the carbons than that of the corresponding protons (Table IV-3) suggests that the interaction involves the π-orbital, which would be in agreement with the earlier quoted findings (19,29-32) that CCl_4 interacts with benzene through a

TABLE IV-3

CCl_4-Induced Deviations from VDWL for Aromatic Compounds and Ethers as Solutes

Compound	Position	$^{13}C\Delta$	$^{1}H\Delta$
C_6H_6		0.33	0.13
CUM	Ci = Cl	0.20	
	C2	0.25	
	C3	0.31	
	C4	0.48	
	average for unsubstituted C	0.35	0.28
MES	Ci = Cl	0.32	
	C2	0.23	0.18
	CH_3	0.31	0.19
m-XYL	Ci = $C_{2,6}$	0.26	
	C_1	0.35	
	C_3	0.20	
	C_4	0.32	
	CH_3	0.31	
DEE	C_α	0.15	
	C_β	0.25	
IPME	OCH_3	0.27	
	C_α	0.24	
	C_β	0.29	
EGDME	C_α	0.03	
	OCH_3	0.29	

charge-transfer interaction. The recorded CCl_4-induced deviations from VDWL can not be attributed to the anisotropic effect of CCl_4. The C-Cl bonds are at an angle of ~ 20° toward the plane of the ring. It may be expected to cause an opposite effect, inducing the shielding of ring carbons (17). In addition, an anisotropic effect could not explain a difference in the chemical shift for substituted and unsubstituted carbons in an axially symmetrical molecule such as mesitylene.

Interactions with Ethers

The IMI between CCl_4 and ethers of low MW are reported to be stronger than van der Waals (31,37-42). Mixing of CCl_4 and aliphatic ethers is endothermic (38,43) as is its mixing with p-dioxane (44-47) and with THF (46). Excess volume of mixing with CCl_4 is negative for p-dioxane (44-48) and even more so for THF (46). CCl_4 and p-dioxane form a solid complex (48).

The IMI between CCl_4 and ethers has been characterized as "halogen bond" (31,49) in which the lone electron pair of oxygen in the ether acts as an n-electron donor to the chlorine (49-51). It has been, however, suggested that the interaction may be more complex, involving simultaneously the interaction with the oxygen, hydrogen bond with electron-deficient hydrogen in ethers and a coulombic interaction with the dipole in the ether (52). Dielectric measurements (32,37) show a molar polarization consistent with the existence of an interaction but UV spectra of ether-CCl_4 mixtures do not show any evidence of

complexes (32,59). CCl_4 dissolved in EGDME and in p-dioxane shows a negligible deshielding, smaller than the one induced by CCl_4 itself. Only somewhat larger is the deshielding induced by THF. (Table IV-1 and Figure IV-1). Those deviations do not give indications of interactions leading to the formation of a strong complex.

CCl_4 dissolved in alkyl ethers shows small upfield deviations from VDWL (Table IV-1 and Figure IV-1). In addition, chemical shifts in symmetrical di-n-alkyl ethers in the Rummens plot form a straight line crossing the VDWL (Figure IV-1). The upfield deviation may indicate either an increase of electron density at the chlorine, happening as a consequence of an IMI or the anisotropic shielding.

Chemical shifts for CCl_4 in mixtures of diethyl ether and n-pentane (Table IV-2 and Figure IV-2) show a linear change with the volume fraction of DEE, suggesting the absence of specific interactions. These results suggest that the deviation for carbon in CCl_4 dissolved in ethers should be attributed to the anisotropic effect of C-O bond (54). Some reports suggest that the intensity of the shielding should be of similar intensity for the two bonds (17), but a definite conclusion on that matter is still to be reached. If the anisotropic effect of C-O bond were somewhat larger than that of the C-C bond, then the linear change of the deviation with the reciprocal volume might be attributed to the difference of the anisotropic effect.

Absolute values for the deviations from VDWL for ethyl, propyl, butyl and pentyl ether show an increase following the increase of Tiffon-Dubois parameter $\mu_2 (V_1^{1/3} + V_2^{1/3})^{-3}$ (55) (Chapter I, Equation

I-8), but not a linear change. This suggests that coulombic interaction is not important between CCl_4 and ethers. DEE, IPME and EGDME dissolved in CCl_4 (Table IV-3) show small to moderate deshielding of all carbons. Methoxy and, more accessible β carbons, are deshielded more than α carbons in both DEE and IPME. The α carbon in EGDME shows only a negligible deshielding. For a carbon to be anisotropically deshielded by CCl_4 it should be positioned along the axis of the C-Cl bond (17). This, in turn is not possible without a specific interaction. For this reason it is believed that CCl_4 induced deshielding reflects the existence of a specific IMI.

The intensity of deshielding of more exposed carbons (0.25 to 0.29 ppm) corresponds to the deshielding CCl_4 induces in $CHCl_3$ (0.23 ppm). Since from the observations of the interaction of the same ethers with $CHCl_3$ we know that both α and β C-H groups may act as proton donors, we may assume that they interact with CCl_4 in the same manner.

Smaller deshielding of the α carbons, which is opposite to what is caused by $CHCl_3$, may be explained by the weakness of the interactions. Since there is no very strong interaction between α hydrogen and CCl_4, molecules interacting with β hydrogens appear to hinder the access of CCl_4 to the α positions.

Since the interaction is weak, CCl_4 is not always interacting at the same position relative to the oxygen in the di-n-alkyl ethers. The increase in the n-alkyl segment then reduces the possibility that CCl_4 is exposed to the anisotropic effect of C-O bond and the positive deviation is vanishing. In the case of EGDME, p-dioxane and THF the

selection of interacting sites is smaller and they are such that they do not allow for the anisotropic effect to exceed the interaction-induced deshielding.

Although the origin of ether-induced deviations on CCl_4 appears to be understandable, the fact that they depend so much on the anisotropy prevents any assessment of the intensity of interaction from them. However, CCl_4-induced deviations on ethers are of the same kind, but considerably stronger than the deviations induced on the ethers by their own cohesive interactions (Chapter VII Tables VII-1 to VII-3). This explains the exothermic mixing of CCl_4 and ethers.

Interactions with Alcohols

The existence of the specific interaction between CCl_4 and alcohols has been reported in several instances. The findings were based on the changes of the heat (56) and volume of mixing (57), vapor-liquid equilibria (58,59), vapor pressure (60), dipole moments (61) and the IR spectra (62-65).

It was suggested that this interaction has the character of the hydrogen bond with CCl_4 acting as acceptor of a hydroxylic proton (9,62-65). Since in two instances with $CHCl_3$ and ethers we have found the evidence suggesting that a hydrogen bond involving $CHCl_3$ is the prevalent mode of interaction, it would be of interest to learn how the chemical shift of CCl_4 reflects an interaction which is believed to be a hydrogen bond.

In Rummens plot CCl_4 dissolved in linear alcohols show small

deshieldings (see Table IV-1 and Figure IV-1). Their intensities decrease with the length of the alkyl segment and reach near zero for 1-dodecanol. Similarly to di-n-alkyl ethers chemical shifts in alchols form a line reaching VDWL. Chemical shifts for CCl_4 in a series of mixtures of n-pentane and 1-propanol do not indicate clearly any preferential solvation of CCl_4 by 1-propanol (Table IV-2 and Figure IV-2). For the first four members of the alcohol series the intensity of the deviations is inversely proportional to their molar volume (Table IV-4 and Figure IV-3). All this suggests that CCl_4 shows only an anisotropically-induced deviation when dissolved in alcohols. The direction of the deviation suggests that its carbon is at, or near, the axis of the O-H or C-O bond of alcohol (54). As mentioned before, such a position is not probable without a specific interaction which holds the molecule in the preferred position. In this case the decrease of deshielding with the length of the chain will only indicate a very weak interaction, whose energy of interaction is of the same order of magnitude as the van der Waals. Deviations induced by methyl, ethyl, and n-propyl alcohol change linearly with the Tiffon-Dubois parameter (55) $\mu_2 \cdot (V_1^{1/3} + V_2^{1/3})^{-3}$ (see Table IV-5 and Figure IV-4). This indicates that CCl_4 has coulombic interaction with those four alcohols in the series. This may be attributed either to a octupole-dipole interaction, or to the C-Cl bond, as a single dipole, interacting with the dipole of the alcohol. This, in turn, may suggest another possible mechanism of the interaction. Hydrogen bonds between molecules of alcohol are very

TABLE IV-4

Alcohol-Induced Deviations from VDWL for CCl_4 as a Function of the Inverse Molar Volume of Solvents

No.	Solvent	V	$10^3/V$	$\Delta\delta$
1	C1OH	40.50	24.69	0.16
2	C2OH	59.67	16.76	0.11
3	C3OH	74.75	13.38	0.08
4	C4OH	91.51	10.93	0.10
5	C5OH	108.69	9.20	0.06
6	C8OH	157.47	6.35	0.03
7	C12OH	227.26	4.40	0.00

Line drawn through experimental points (except C4OH and C12OH) has the correlation 0.9961 for the equation

$$\Delta\delta = -9.62 + 6.94\ (\tfrac{1}{V}),\ \text{ppm}$$

and average deviation of 0.0043 ppm.

Fig. IV-3. Relationship between the alcohol-induced deviation from van der Waals line for carbon tetrachloride and molar volume of alcohols.

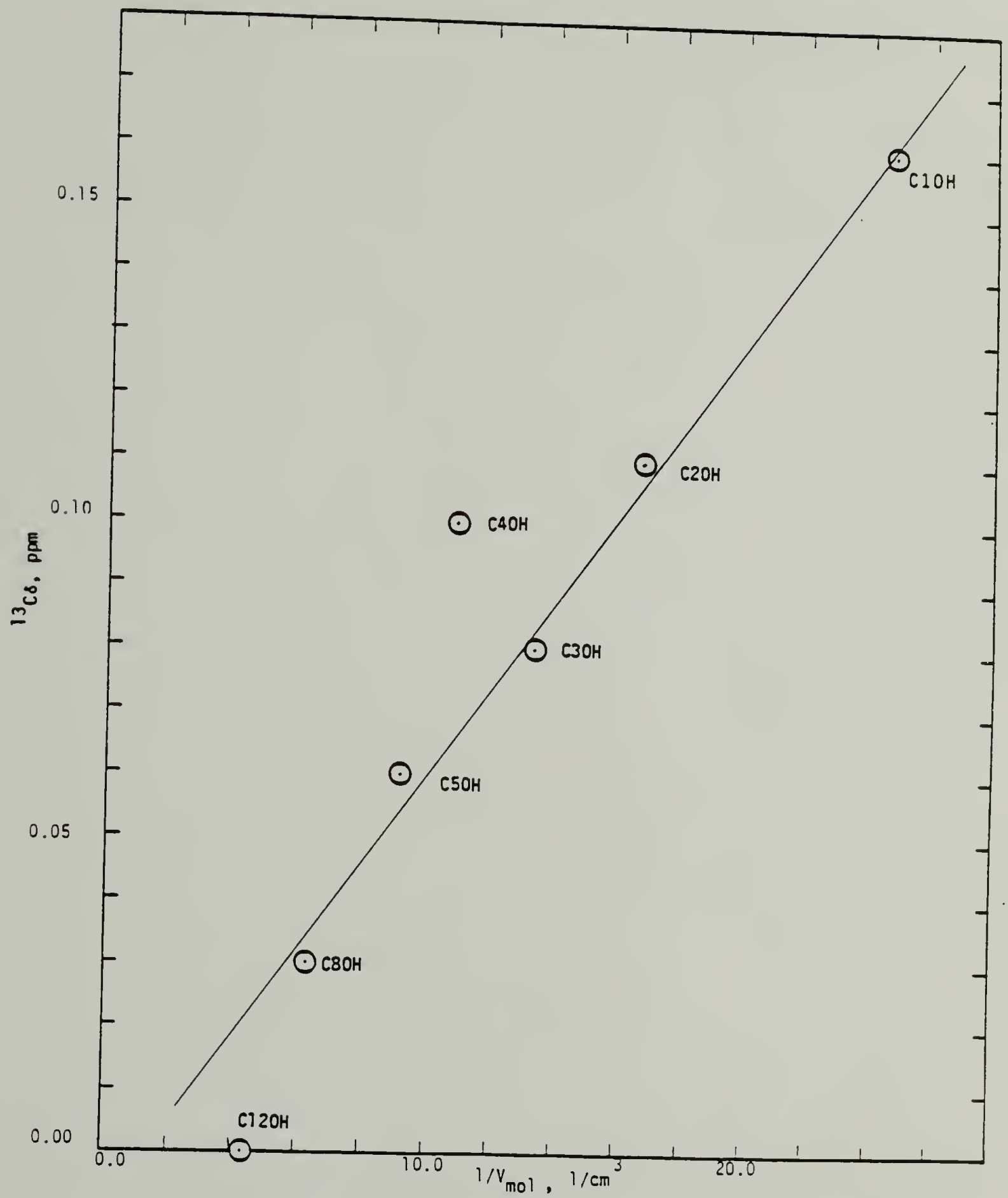

0.15
0.10
0.05
0.00
$^{13}C\delta$, ppm
C10H
C20H
C40H
C30H
C50H
C80H
C120H
0.0
10.0
20.0
$1/V_{mol}$, $1/cm^3$

TABLE IV-5

Alcohol-Induced Deviation from VDWL for CCl_4 as a Function of the Cans-Tiffon Parameter*

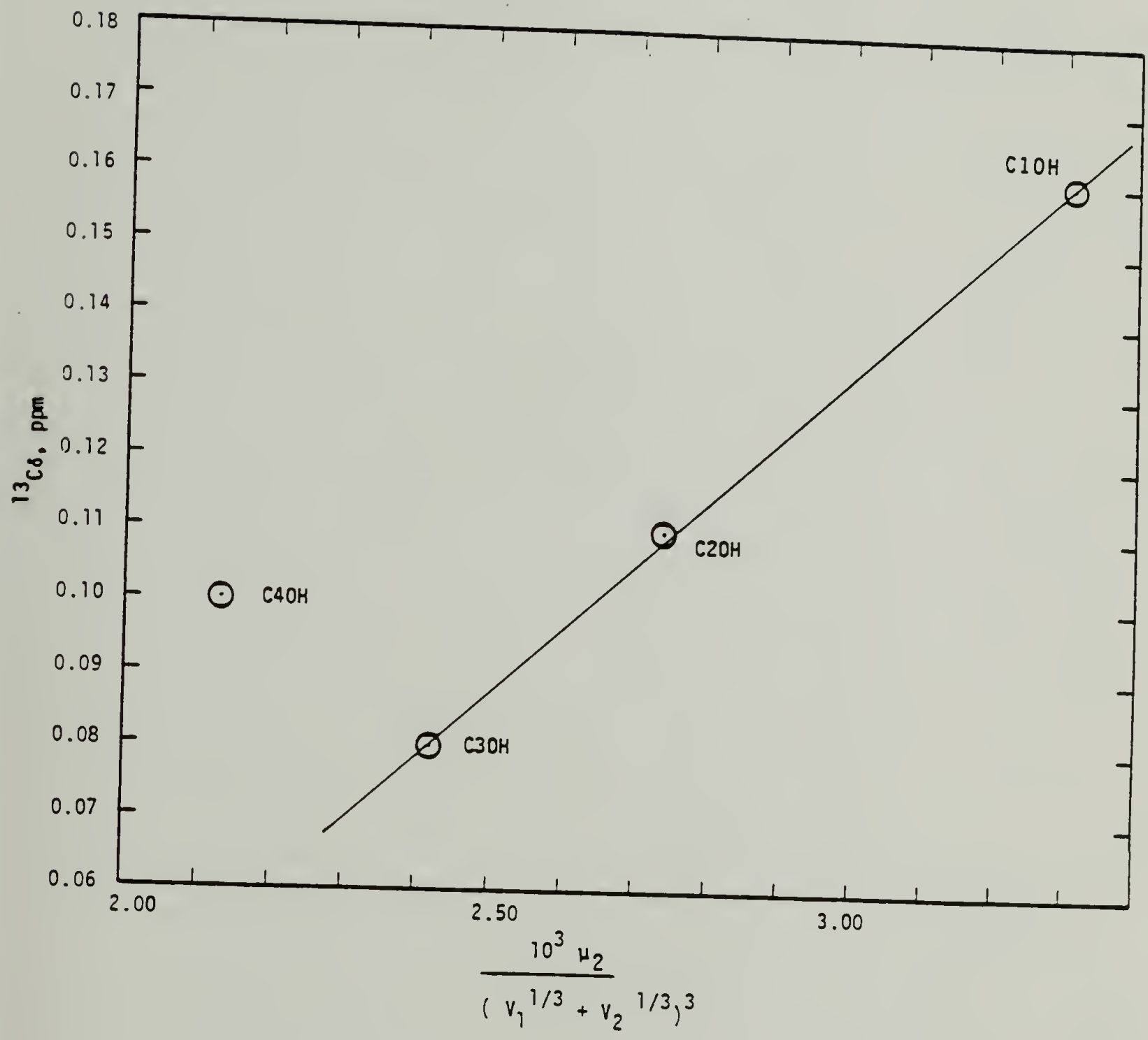
Solvent	μ**	V_2	$\frac{\mu_2 \cdot 10^3}{(V_1^{1/3} + V_2^{1/3})^3}$	Δδ
C1OH	1.71	40.50	3.31	0.16
C2OH	1.68	59.67	2.74	0.11
C3OH	1.65	74.75	2.42	0.08
C4OH	1.60	91.51	2.13	0.10

*Molar volume of CCl_4 is 96.50 ml/gmol. For 3 points correlation is 0.9998 and the equation of the line is

$$\Delta\delta = -0.136 + 89.63\ \mu_2 \cdot (V_1^{1/3} + V_2^{1/3})^{-3}\ \text{(ppm)}$$

**Values from the reference (67).

Fig IV-4. Relationship between the alcohol-induced deviation from van der Waals line for carbon tetrachloride and coulombic force parameter.


0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
$^{13}C\delta$, ppm
C1OH
C2OH
C3OH
C4OH
2.00
2.50
3.00
$\frac{10^3 \mu_2}{(V_1^{1/3} + V_2^{1/3})^3}$

strong (66). It is possible that CCl_4 can not break any of them since its electron donating power is considerably smaller than that of the oxygen. The alkyl segment of every alcohol is, however, polarized by the attached hydroxyl group and may be considered a dipole whose moment is related to the dipole moment of the alcohol molecule. In such a case, alcohols which are mutually interconnected, through hydrogen bonds of their hydroxy groups, still may interact with CCl_4 as dipole.

At present, based solely on chemical shifts for CCl_4 it is not possible to determine the nature of this interaction any closer. Additional study of this subject, involving NMR of alcohols and possibly IR spectra, is necessary. It should be determined whether alcohols interact through hydrogens (and through which ones) or through oxygen.

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C H A P T E R V

INTERMOLECULAR INTERACTIONS OF TRICHLOROETHYLENE AND TETRACHLOROETHYLENE

Introduction

There are not many reports in the literature concerned with the IMI between trichloroethylene, C_2HCl_3,or tetrachloroethylene, C_2Cl_4, and other organic compounds.

Rummens plots of the chemical shifts for both compounds in n-alkanes show straight lines with good correlations (Tables V-1 to V-3 and Figures V-1 to V-4). For C_2HCl_4 the slope, Si, of carbon VDWL is 71.24 ppm. The C_2HCl_3 has a similar Si = 70.69 ppm for CCl_2 carbon and Si = 50.21 ppm for the CHCl carbon. The hydrogen from C_2HCl_3 has Si = 42.12 ppm which is only a small reduction (~ 11%) from the slope for $CHCl_3$.

At this moment the full importance of these values is not known. It appears important, however, to note that similar functional groups in different molecules do show almost identical slopes of VDWL. This seems to support the opinion, mentioned in Chapter I (1) that the Onsager reaction field has to be defined only for one separate segment of the molecule.

Hydrogen from C_2HCl_3 dissolved in cyclohexane shows only a negligible shielding (-0.06). Its intensity indicates the absence of any specific interaction between the two compounds.

TABLE V-1

^{13}C NMR Chemical Shifts for Tetrachloroethylene in Different Solvents*

No.	Solvent	g^2	δcorr	δVDWL	Δδ
1	C6	3.47	52.72		
2	C7	3.63	52.83		
3	C8	3.78	52.93		
4	C9	3.87	53.00		
5	C10	3.96	53.07		
6	C16	4.26	53.28		
7	C_2Cl_4	5.24	53.36	53.98	-0.62
8	CCl_4	4.62	53.55	53.54	0.01
9	$CHCl_3$	4.43	53.71	53.40	0.31
10	CH_2Cl_2	4.13	53.74	53.19	0.55
11	DEE	3.15	52.66	52.49	0.17
12	IPME	3.24	52.83	52.55	0.28
13	DIPE	3.38	52.65	52.65	0.00
14	EGDME	3.52	53.48	52.75	0.73
15	p-DIOX	4.09	54.10	53.16	0.94
16	C_6H_6	5.17	52.83	53.93	-1.10
17	CUM	5.05	53.02	53.84	-0.82
18	MES	5.13	53.19	53.90	-0.71
19	(50 vol % C16+50 Vol % Benz)		52.99		

*All values at 34 ± 0.5°C relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (See Appendix, Table A-3). Symbols as in Appendix, Table A-1.

**Van der Waals line has the correlation 0.9998 for the equation

$$\delta = 50.24 + 71.24\ g^2 \text{ (ppm)}.$$

Fig. V-1. Rummens plot for ^{13}C NMR chemical shifts of tetrachloroethylene in different solvents.

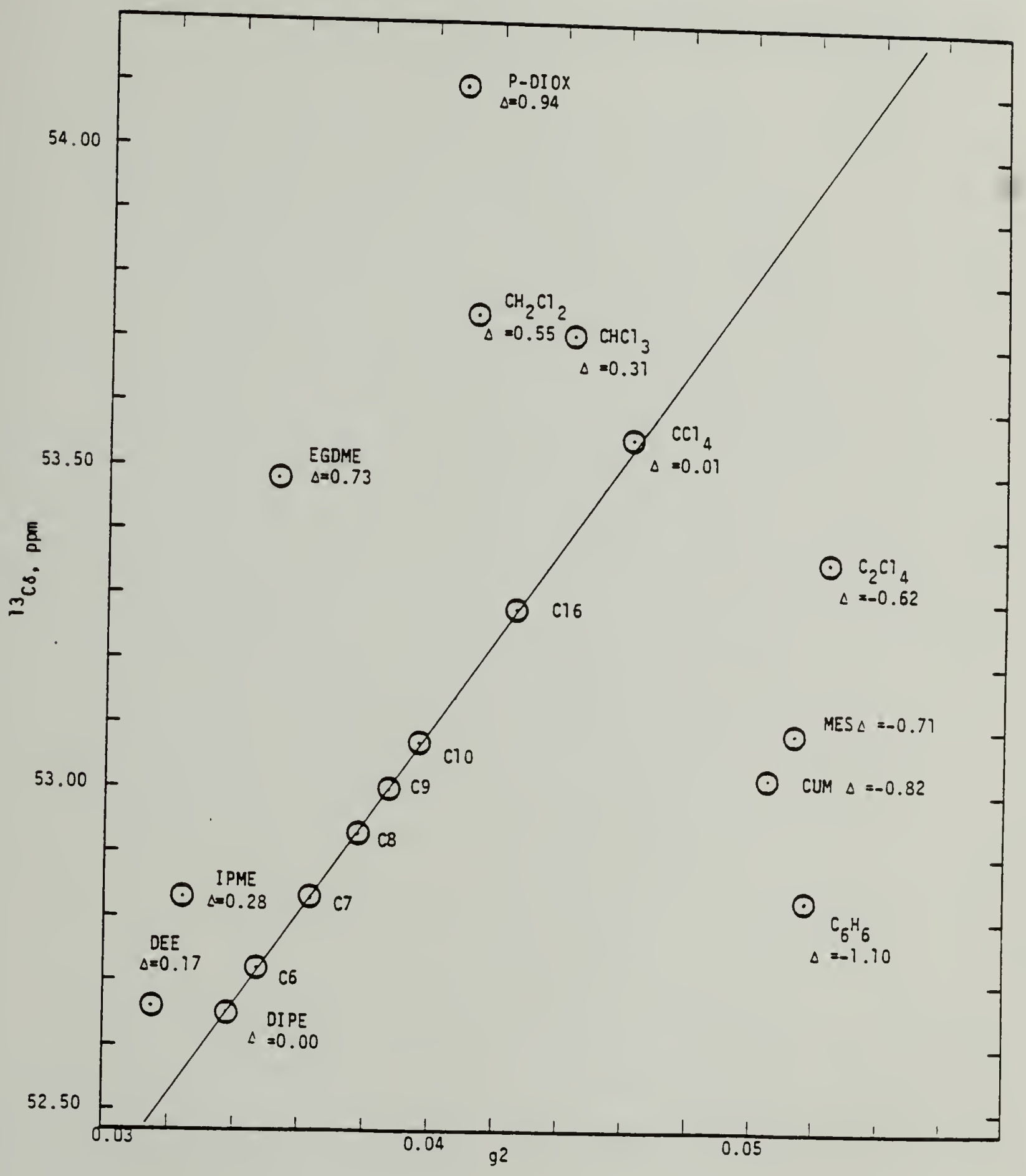

P-DIOX
Δ=0.94
54.00
CH_2Cl_2
Δ =0.55
$CHCl_3$
Δ =0.31
CCl_4
Δ =0.01
53.50
EGDME
Δ=0.73
C_2Cl_4
Δ =-0.62
$^{13}C\delta$, ppm
C16
C10
C9
C8
MES Δ =-0.71
53.00
CUM Δ =-0.82
IPME
Δ=0.28
C7
C_6H_6
Δ =-1.10
DEE
Δ=0.17
C6
DIPE
Δ =0.00
52.50
0.03
0.04
0.05
g2

TABLE V-2

^{13}C NMR Chemical Shifts for Trichloroethylene in Different Solvents[a]

No	Solvent	g^2	CCl_2 δcorr	CCl_2 δVDWL	CCl_2 Δ	CHCl δcorr	CHCl δVDWL	CHCl Δ
1	C5	3.24	56.47[b]			48.35[b]		
2	C6	3.47	56.61[b]			48.53[b]		
3	C7	3.63	56.69[b]			48.64[b]		
4	C7	3.63	56.69[b]			48.61[b]		
5	C7	3.63	56.67[b]			48.60[b]		
6	C7	3.63	56.66[b]			48.63[b]		
7	C8	3.78	56.76[b]			48.69[b]		
8	C8	3.78	56.74[b]			48.74[b]		
9	C8	3.78	56.76[b]			48.72[b]		
10	C9	3.87	56.79[b]			48.82[b]		
11	C10	3.96	56.88[b]			48.84[b]		
12	C16	4.26	56.97[b]			49.06[b]		
13	C16	4.26	57.00[b]			49.09[b]		
14	C_2HCl_3	4.86	56.80	57.30	-0.50	49.44	49.49	-0.05
15	C_2HCl_3	4.86	56.85	57.30	-0.45	49.45	49.49	-0.04
16	C_2HCl_3	4.86	56.81	57.30	-0.49	49.42	49.49	-0.07
17	DEE	3.15	55.59	56.44	-0.85	49.59	48.28	1.31
18	DEE	3.15	55.58	56.44	-0.86	49.60	48.28	1.32
19	DEE	3.15	55.59	56.44	-0.85	49.59	48.28	1.31
20	DEE	3.15	55.58	56.44	-0.86	49.60	48.28	1.32
21	IPME	3.24	55.44	56.48	-1.04	49.75	48.35	1.40
22	IPME	3.24	55.44	56.48	-1.04	49.75	48.35	1.40
23	DIPE	3.38	55.71	56.55	-0.84	49.55	48.45	1.10
24	DIPE	3.38	55.71	56.55	-0.84	49.55	48.45	1.10
25	EGDME	3.52	55.50	56.63	-1.13	50.48	48.50	1.98
26	p-DIOX	4.09	56.17	56.91	-0.74	50.42	48.95	1.47
27	p-DIOX	4.09	56.17	56.91	-0.74	50.42	48.95	1.47
28	C_6H_6	5.17	55.86	57.45	-1.59	49.18	49.71	-0.53
29	TOL	5.12	55.96	57.43	-1.47	49.17	49.68	-0.51
30	CUM	5.05	56.65	57.39	-0.74	49.31	49.63	-0.32
31	MES	5.13	56.81	57.43	-0.62	49.30	49.68	-0.38
32	{50 vol % C16 + 50 vol % Benz}	--	56.25	--	---	49.16	---	--

[a]All values at 31 ± 0.5°C relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagentic susceptibility (see Appendix, Table A-3). Symbols as in Appendix, Table A-1.

[b]Van der Waals line for CCl_2 carbon has the correlation 0.9934 for the equation

$$\delta = 54.86 + 50.21\ g^2 \text{ (ppm)}$$

Van der Waals line for CHCl carbon has the correlation 0.9952 for the equation

$$\delta = 46.06 + 70.69\ g^2 \text{ (ppm)}.$$

Fig. V-2. Rummens plot for ^{13}C NMR chemical shifts for CCl_2 carbon of trichloroethylene in different solvents.

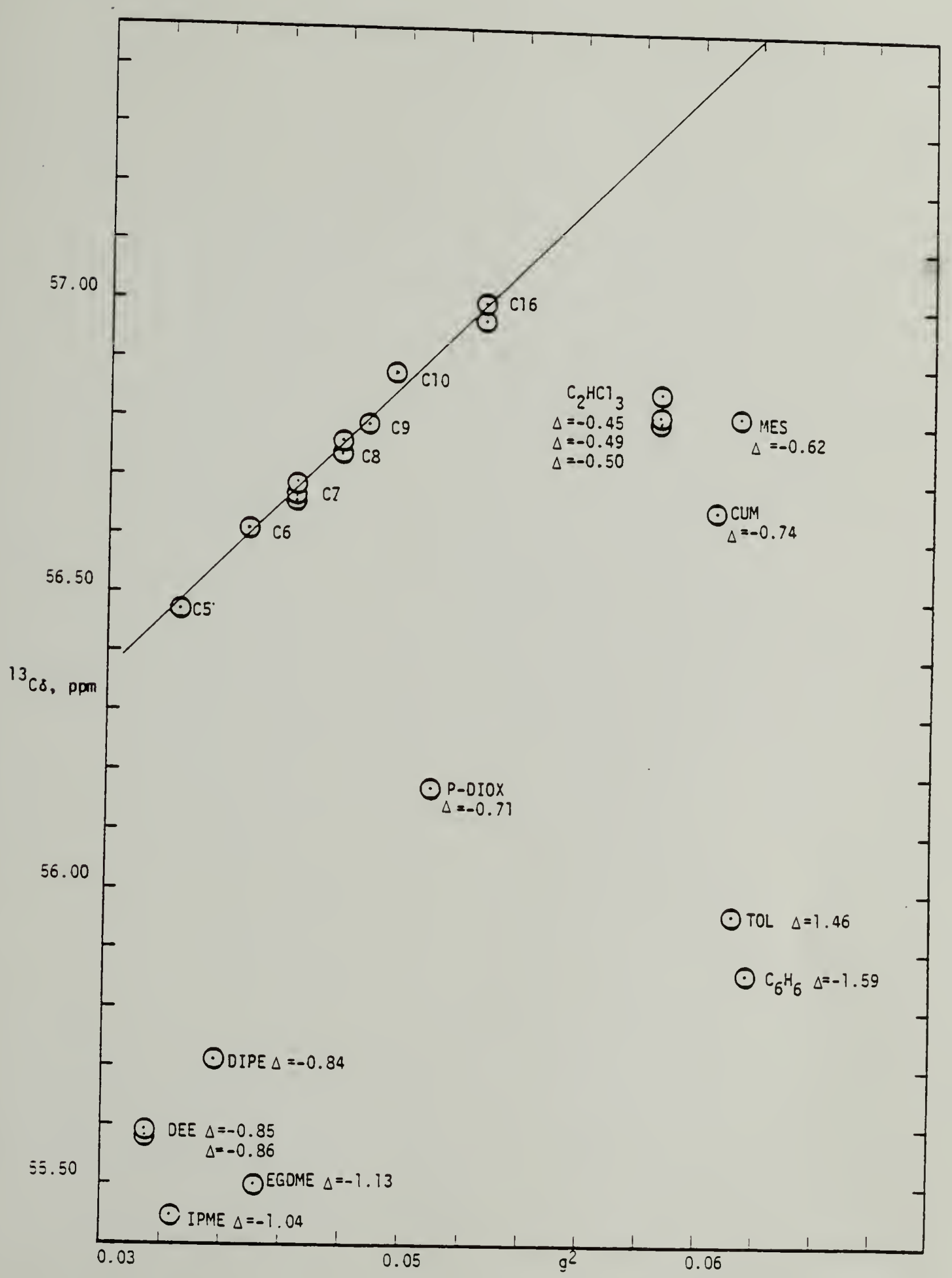

57.00
56.50
56.00
55.50
$^{13}C\delta$, ppm
0.03
0.05
g^2
0.06
C16
C10
C9
C8
C7
C6
C5
C_2HCl_3
Δ =-0.45
Δ =-0.49
Δ =-0.50
MES
Δ =-0.62
CUM
Δ =-0.74
P-DIOX
Δ =-0.71
TOL Δ=1.46
C_6H_6 Δ=-1.59
DIPE Δ =-0.84
DEE Δ=-0.85
Δ=-0.86
EGDME Δ=-1.13
IPME Δ=-1.04

Fig. V-3. Rummens plot for ^{13}C NMR chemical shifts for CHCl carbon of trichloroethylene in different solvents.

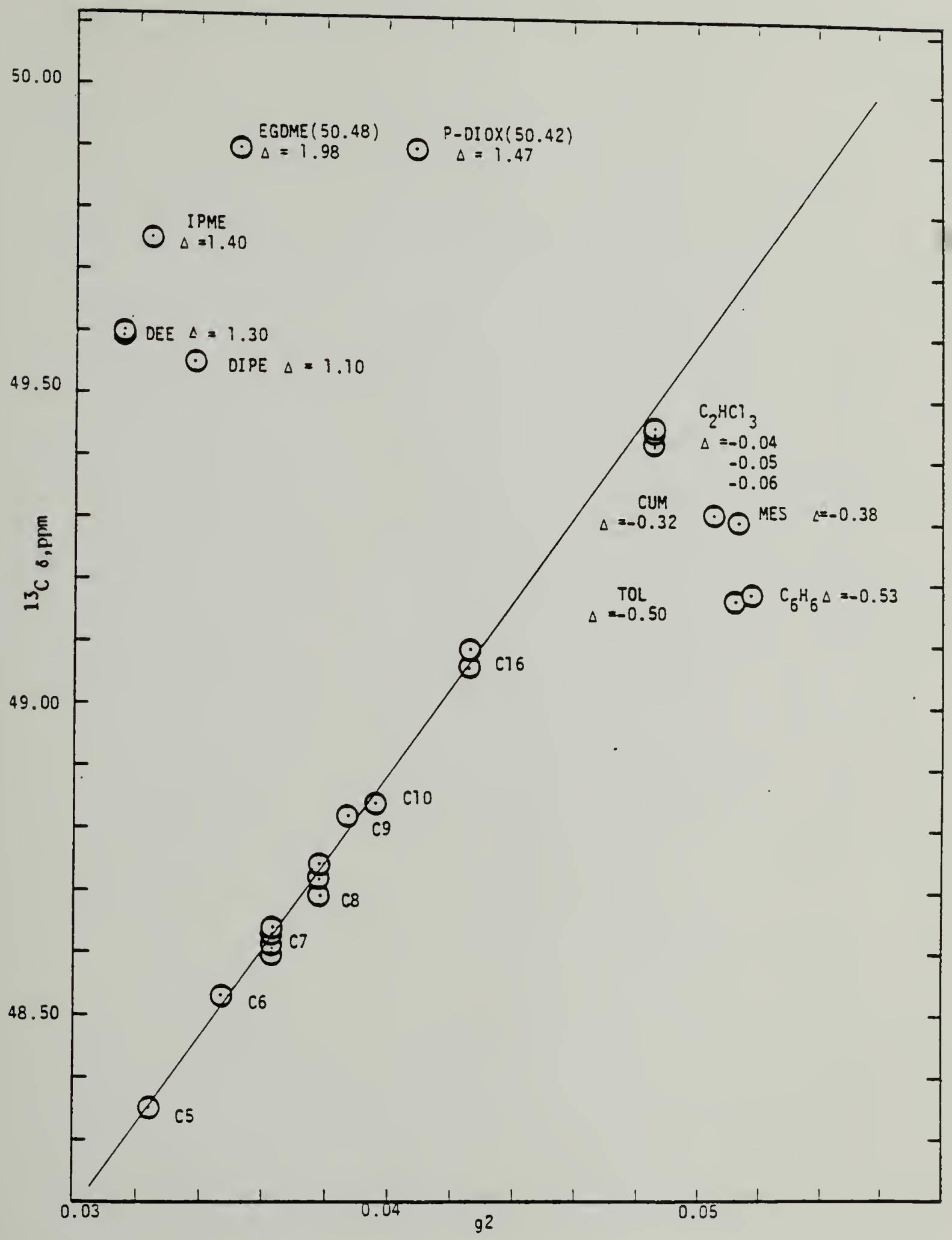

50.00
49.50
49.00
48.50
^{13}C δ,ppm
EGDME(50.48)
Δ = 1.98
P-DIOX(50.42)
Δ = 1.47
IPME
Δ =1.40
DEE Δ = 1.30
DIPE Δ = 1.10
C_2HCl_3
Δ =-0.04
-0.05
-0.06
CUM
Δ =-0.32
MES Δ=-0.38
TOL
Δ =-0.50
C_6H_6 Δ =-0.53
C16
C10
C9
C8
C7
C6
C5
0.03
0.04
0.05
g2

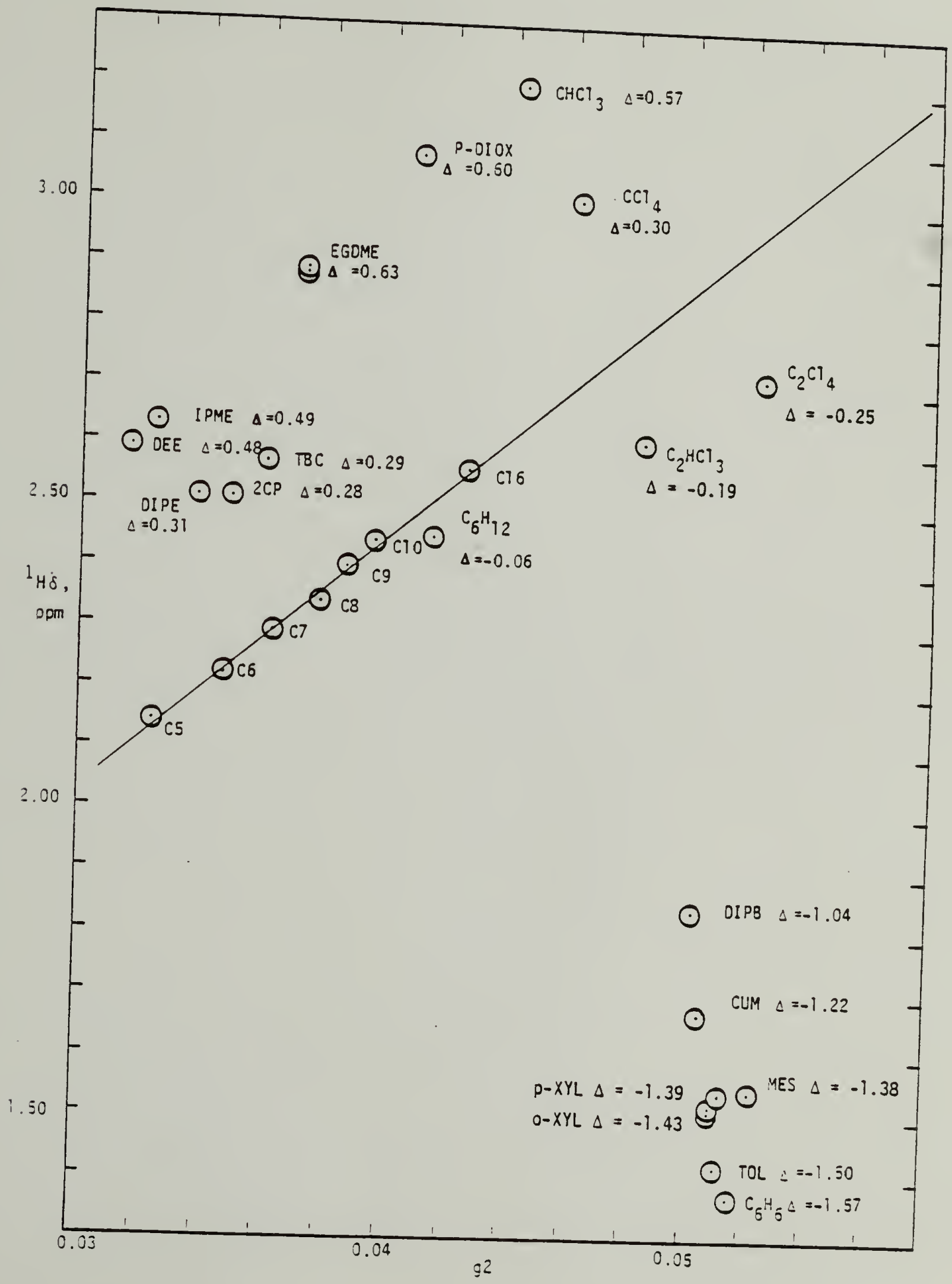
TABLE V-3

^{1}H NMR Chemical Shifts for Trichloroethylene in Different Solvents[a]

No	Solvent	g^2	δcorr	δVDWL	Δ
1	C5	3.24	2.14[b]		
2	C6	3.47	2.22[b]		
3	C7	3.63	2.29[b]		
4	C8	3.78	2.34[b]		
5	C9	3.87	2.40[b]		
6	C10	3.96	2.44[b]		
7	C16	4.26	2.56[b]		
8	C16	4.26	2.56[b]		
9	C16	4.26	2.56[b]		
10	C_6H_{12}	4.15	2.45	2.51	-0.06
11	C_2HCl_3	4.84	2.61	2.80	-0.19
12	C_2Cl_4	5.24	2.72	2.97	-0.25
13	CCl_4	4.62	3.01	2.71	0.30
14	$CHCl_3$	4.43	3.20	2.63	0.57
15	2CP	3.51	2.55	2.24	0.31
16	TBC	3.60	2.57	2.28	0.29
17	DEE	3.16	2.59	2.10	0.49
18	IPME	3.24	2.63	2.13	0.50
19	DIPE	3.38	2.51	2.19	0.32
20	EGDME	3.52	2.88	2.25	0.63
21	EGDME	3.52	2.89	2.25	0.64
22	p-DIOX	4.09	3.08	2.49	0.59
23	C_6H_6	5.17	1.37	2.94	-1.57
24	C_6H_6	5.17	1.37	2.94	-1.57
25	TOL	5.12	1.42	2.92	-1.50
26	CUM	5.05	1.67	2.89	-1.22
27	o-XYL	5.23	1.54	2.97	-1.43
28	p-XYL	5.10	1.52	2.91	-1.39
29	p-XYL	5.10	1.52	2.91	-1.39
30	MES	5.13	1.54	2.92	-1.38

[a]All values at 37 ± 0.5°C, relative to the external standard (10 vol % H_2O in $DMSOd_6$), corrected for diamagnetic susceptibility (See Appendix, Table A-3). Symbols as in Appendix, Table A-1.
[b]Van der Waals line has the correlation 0.9986 for the equation:
$\delta = 0.76 + 42.12\ g^2$ (ppm).

Fig. V-4. Rummens plot for ^{1}H NMR chemical shifts of trichloroethylene in different solvents.


CHCl3 Δ=0.57
P-DIOX Δ=0.60
CCl4 Δ=0.30
EGDME Δ=0.63
C2Cl4 Δ = -0.25
IPME Δ=0.49
DEE Δ=0.48
TBC Δ=0.29
2CP Δ=0.28
C2HCl3 Δ = -0.19
DIPE Δ=0.31
C16
C6H12 Δ=-0.06
C10
C9
C8
C7
C6
C5
DIPB Δ=-1.04
CUM Δ=-1.22
p-XYL Δ = -1.39
o-XYL Δ = -1.43
MES Δ = -1.38
TOL Δ=-1.50
C6H6 Δ=-1.57
3.00
2.50
2.00
1.50
1Hδ, ppm
0.03
0.04
0.05
g2

In order to understand the deviations induced by the cohesive interactions in C_2Cl_4 and C_2HCl_3 it is necessary to understand first their interactions with chloroform, $CHCl_3$.

C_2Cl_4 dissolved in $CHCl_3$ shows deshielding of 0.30 ppm, suggesting a weak IMI. $CHCl_3$ dissolved in C_2Cl_4 (Table V-5) shows shieldings of -0.18 ppm on the hydrogen and -0.36 ppm on the carbon. The direction of the deviation indicates the anisotropic effect of either double or C-Cl bond (2,3). However the weaker shielding of the hydrogen suggests that it may be engaged in an IMI inducing deshielding. This identifies the IMI between $CHCl_3$ and C_2Cl_4 as a weak hydrogen bond in which C_2Cl_4 acts as an electron donor.

$CHCl_3$ dissolved in C_2HCl_3 shows (Table V-4) weak upfield deviations: -0.12 ppm for hydrogen and -0.10 ppm for its carbon. The anisotropic shielding by C_2HCl_3 which is considerably smaller than the one by C_2Cl_4 may be explained as the presence of a stronger IMI deshielding $CHCl_3$. Its character may again be a hydrogen bond.

Pure C_2Cl_4 shows an upfield deviation of -0.64 ppm. Its intensity reminds very much of the C_2Cl_4 induced deviations on β carbons in DEE and IPME (-0.64 and -0.63 ppm respectively) and on the methyl carbon in mesitylene (-0.56 ppm) (Table V-5). The last of those interactions cannot be much stronger than a van der Waals IMI.

Interestingly enought C_2HCl_3 induced deviations on the same carbons are -0.65, -0.59 and -0.57 ppm (for βC in DEE, βC in IPME and $-CH_3$ in mesitylene, respectively) (Table V-4). We may then assume that this level of shielding (-0.55 to -0.65 ppm) is the typical ani-

TABLE V-4

Trichlorethylene-Induced Deviations from VDWL for Different Compounds

Compound	Carbon	$^{13}C\Delta$	$^{1}H\Delta$
$CHCl_3$	--	-0.10	-0.12
DEE	α	-0.29	
	β	-0.65	
IPME	OCH_3	-0.46	
	α	0	
	β	-0.59	
EGDME	OCH_3	-0.31 (0.74)	
	Average	0.52	
	α	-0.47	
C_6H_6	--	-0.22	-0.16
CUM	Ci = Cl	0.07	
	C2	-0.22	
	C3	-0.15	
	C4	-0.21	
	Average	-0.19	-0.06
MES	Ci = Cl	0.23	
	C2	-0.28	-0.21
	CH_3	-0.57	-0.25

TABLE V-5

Tetrachloroethylene-Induced Deviations from VDWL for Different Compounds

Compound	Carbon	$^{13}C\Delta$	$^{1}H\Delta$
$CHCl_3$	--	-0.30	-0.18
DEE	α	-0.39	
	β	-0.64	
IPME	$-OCH_3$	-0.48	
	α	-0.26	
	β	-0.63	
EGDME	$-OCH_3$	-0.52	
	α	-0.39	
C_6H_6	--	-0.47	-0.42
CUM	Ci	-0.33	
	Co	-0.41	
	Cm	-0.39	
	Cp	-0.41	
	Average	-0.40	-0.12
MES	Ci	-0.15	
	Co	-0.48	-0.31
	$-CH_3$	-0.50	-0.30

sotropic effect of C_2Cl_4 and C_2HCl_3 on nonpolar solutes. This deviation is stronger than reported anisotropic effects of the double (2) or C-Cl bond (3). It may be attributed to a cumulative effect of both the double (2) and C-Cl bond (3). Since this intensity of shielding by C_2Cl_4 appears on nonpolar solutes it may be assumed that the cohesive interaction of C_2Cl_4 does not have any strong, specific IMI. Pure C_2HCl_3 induces only a negligible upfield deviation (-0.05 ppm) for CHCl carbon and a strong shielding (-0.51 ppm) for CCl_2 carbon. Deviation for hydrogen is -0.18 ppm, somewhat stronger than the one that C_2HCl_3 induces for $CHCl_3$ (-0.12 ppm) but somewhat weaker than the shielding C_2HCl_3 shows when dissolved in C_2Cl_4 (-0.23 ppm). From the differences in chemical shifts of hydrogen and from the strong deshielding of CHCl carbon it is apparent that C_2HCl_3 has a cohesive interaction which is inducing deshielding of CHCl group. This is probably a hydrogen bond. Judging from changes in hydrogen shifts, this IMI is weaker than IMI between C_2HCl_3 and $CHCl_3$ or cohesive IMI of $CHCl_3$ itself.

Interaction with Ethers

Mixing of C_2HCl_3 with ethers is reported as weakly endothermic (4). Mixtures have an excess glass temperature, whose maximum is at 50 molar % of C_2HCl_3 (5,6). The excess is ~ 12°C for diisopropyl ether, DIPE, and ~ 16° for diethyl ether, DEE, or tetrahydrofuran THF. The interaction is believed to be a hydrogen bond with C_2HCl_3 as proton donor. It is found to be a weaker proton donor than $CHCl_3$ or

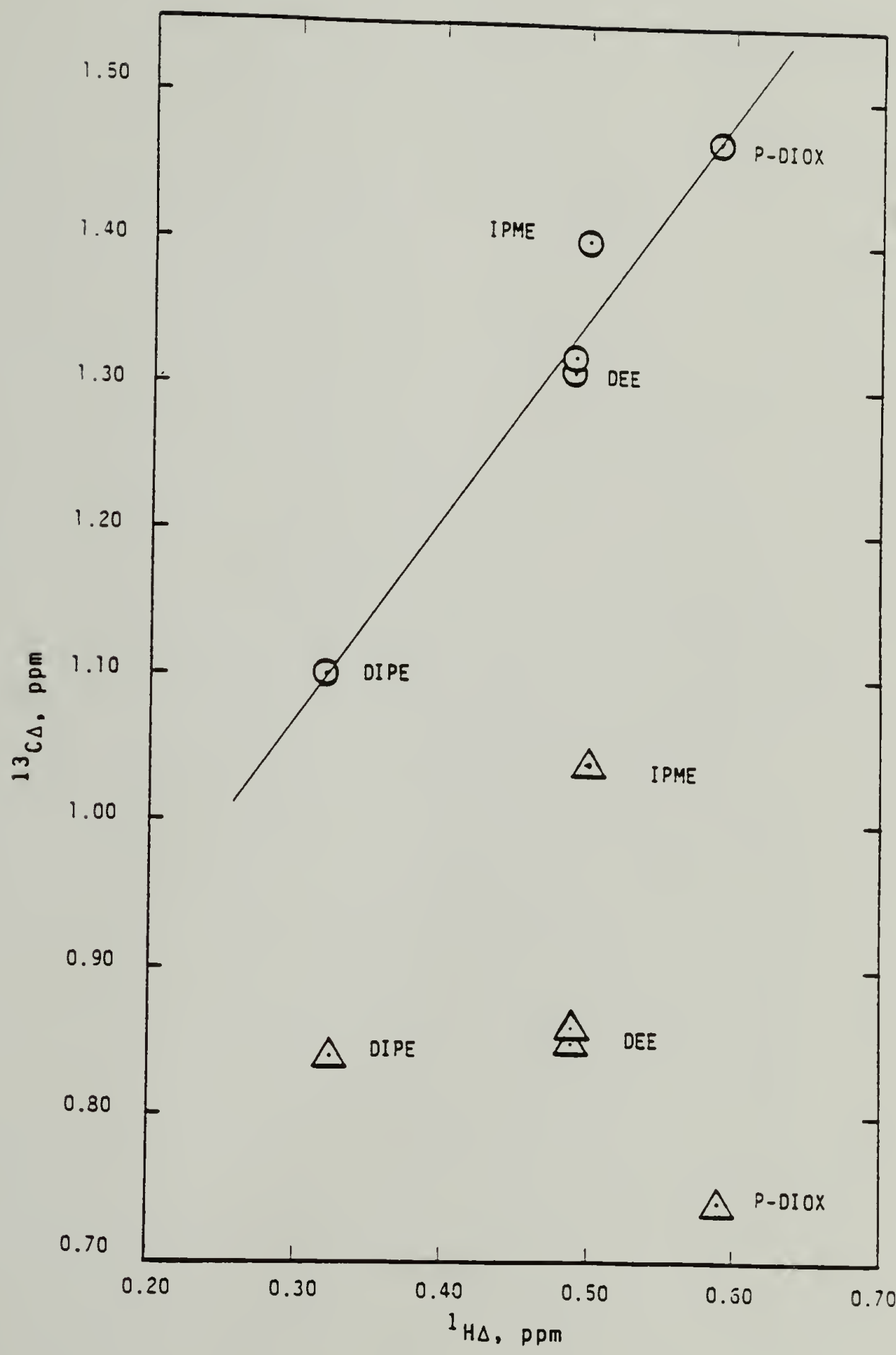
dichloromethane (5,6). In the Rummens plot (Figures V-2 to V-4) deviations induced by ethers are downfield for proton and for proton-bearing carbon. This indicates hydrogen bonding. The ^{1}H and ^{13}C deviations for CHCl group in DEE, IPME, DIPE and p-dioxane show mutual correlation (Table V-6 and Figure V-5). This correlation is also indicating a hydrogen bond. However the CCl_2 carbon shows a strong shielding induced by ethers (Figure V-2). A similar effect has been reported by Cans, Tiffon and Dubois (7) for alkyl substituted ethenes. In polar solvents the electron rich (di-alkyl substituted) sp^2 carbons show downfield deviations from VDWL while the electron poor (unsubstituted) carbons show upfield deviations. The downfield deviations were considerably larger than the upfield ones. This was attributed to the involvement of the double bond as electron donor. In the case of trichloroethylene the reason for this shielding may be sought in the large polarizability of the double bond (8) and in dipolar character of the hydrogen bond interaction (9-11). When the electron deficient hydrogen on sp^2 approaches an electron donor this induces the polarization which results in an increased shielding of the carbon at the other end of the double bond. C_2HCl_3 as solvent causes upfield deviations for all carbons of ethers (Table V-4). A characteristic pattern is that all carbons nearer to the oxygen show a smaller shielding. In IMPE the α carbon is completely unaffected. This pattern might be explained if it is assumed that C_2HCl_3 interacts with the oxygen in ethers, thus holding a fixed point of rotation from which it induces the anisotropic effect. Meanwhile aliphatic ethers

TABLE V-6

Ether-Induced ^{1}H and ^{13}C Deviations from VDWL for Trichloroethylene

No.	Solvent	$^{1}H\Delta$ CHCl	$^{13}C\Delta$ CHCl	$^{13}C\Delta$ CCl_2
1	DEE	0.48	1.30	-0.85
2	DEE	0.48	1.31	-0.86
3	IPME	0.49	1.40	-0.84
4	DIPE	0.31	1.10	-0.84
5	p-DIOX	0.60	1.47	-0.71

Fig. V-5. Relationships between the ^{13}C NMR and ^{1}H NMR deviations from Van der Waals lines for trichloroethylene: (○) CHCl carbon; (△) CCl_2 carbon.


1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
$^{13}C\Delta$, ppm
P-DIOX
IPME
DEE
DIPE
IPME
DIPE
DEE
P-DIOX
0.20
0.30
0.40
0.50
0.60
0.70
$^{1}H\Delta$, ppm

induce deshielding of the carbon in C_2Cl_4 which suggests that it is engaged as n-electron donor with electron deficient hydrogens. (A charge transfer complex would induce a shielding of Cl and a transmitted shielding of carbon in C_2Cl_4 (12).) However ethers dissolved in C_2Cl_4 show shielding of all the carbons whose pattern is almost identical with the one induced by C_2HCl_3 (Tables V-4 and V-5). The only differences are in α carbons in IPME and to some extent, in EGDME.

Both C_2HCl_3 and C_2Cl_2 show ether-induced deviations which are strong enough to indicate the specific interactions which are of different nature. The possible explanation for their similar effect on ethers is in the low intensity of the specific IMI. In that case their effect on the chemical shift of ethers would be completely masked by the anisotropic effect.

Hydrogen in C_2HCl_3 has a similar slope of VDWL as the hydrogen in $CHCl_3$ and this way be applied to make a crude estimate of the intensity of the interaction between C_2HCl_3 and ethers. Comparing values in Tables III-2 and V-3 (Table V-7) it may be seen that hydrogen in C_2HCl_3 shows 9 to 50% smaller deviation from VDWL than the hydrogen in $CHCl_3$. It is noticed that the ^1H deviation of C_2HCl_3 is reduced particularly strongly when access to the oxygen is hindered. This agrees with the previous assumption that C_2HCl_3 acts as proton donor toward ethers and indicates that it is a poorer proton donor than $CHCl_3$.

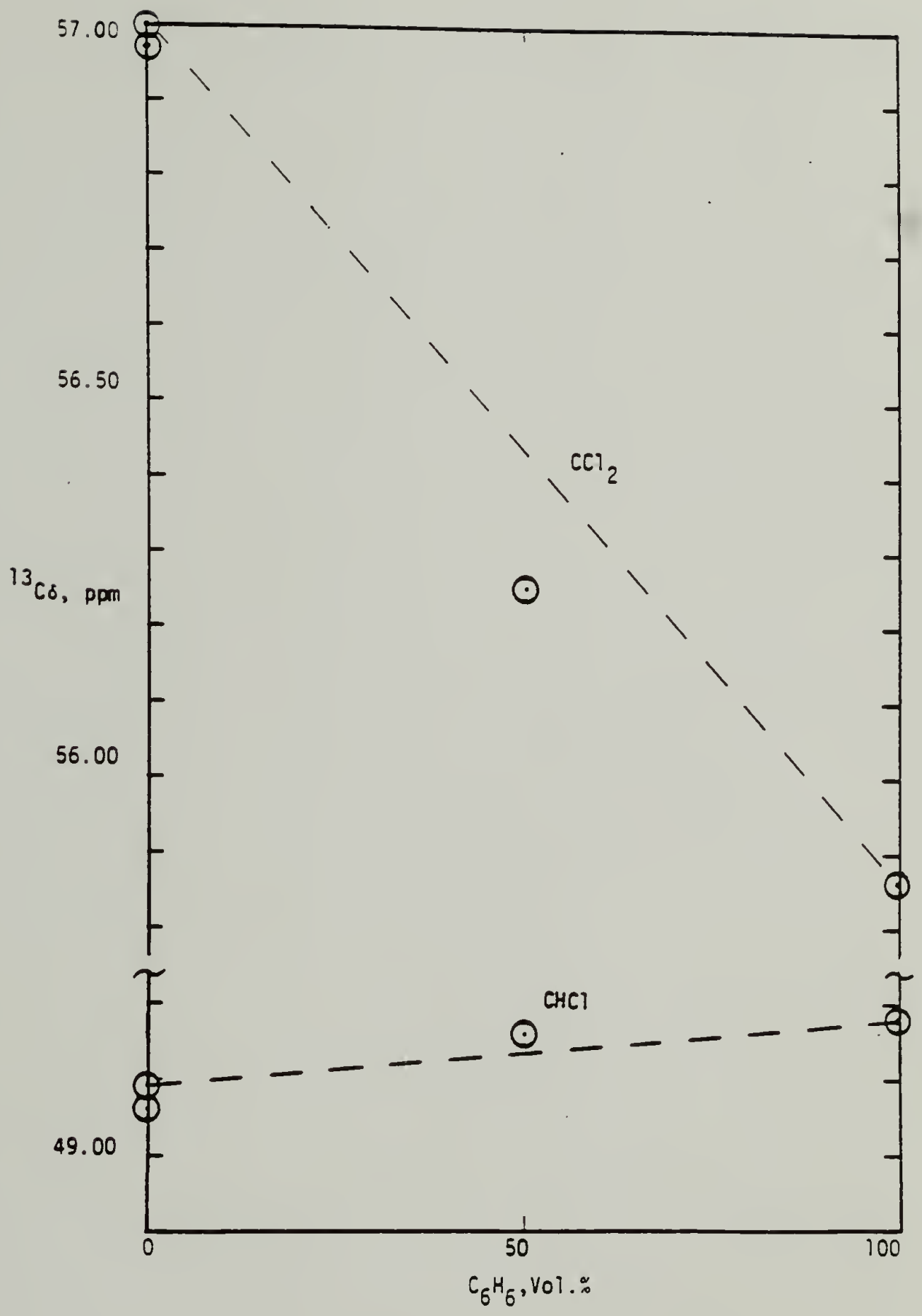
At present we do not have data which may allow such an estimate

TABLE V-7

Ether-Induced ^1H Deviations From VDWL for Chloroform and Trichloroethylene

Solvent	$CHCl_3$	C_2HCl_3	Difference
p-DIOX	0.65	0.59	9%
EGDME	0.85	0.63	26%
IPME	0.69	0.50	28%
DEE	0.79	0.49	38%
DIPE	0.65	0.32	51%

Fig. V-6. The ^{13}C NMR chemical shifts of trichloroethylene in mixtures of n-hexadecane and benzene.


57.00
56.50
56.00
49.00
$^{13}C\delta$, ppm
CCl_2
CHCl
0
50
100
C_6H_6, Vol.%

for C_2Cl_4. However the intensity of ether-induced deviation appears to be very much related to the accessibility of the most polarized C-H bonds. It drops sharply from p-dioxane to DEE and becomes zero for DIPE, which suggests very weak interactions.

Interaction with Aromatic Compounds

Cosolution of benzene (10^{-3} molar) and C_2HCl_3 (10^{-1} molar) in an inert solvent shows a change of benzene's UV spectrum indicating the existence of a π-hydrogen bond (13). The same interpretation has been given for the change of ^1H NMR chemical shift of C_2HCl_3 dissolved in a series of mixtures of benzene and cyclohexane (14). The enthalpy of this interaction has been determined to be $\Delta H = -1.38 \pm 0.09$ kcal/mole (14). This is in agreement with an early experimental finding that the excess heat of mixing of the two compounds is near zero (4) and with the very small effect of added C_2HCl_3 on the T_g of toluene (6).

Our NMR results indicate that aromatic solvents induce very large shielding of the proton (Table V-3) and of the dichloro-substituted carbon in C_2HCl_3. Only medium-to-small shielding is, however, seen on the hydrogen-bearing carbon (Table V-2). An explanation similar to that offered for ether solutions of C_2HCl_3 seems applicable here too. Apparently, the very mobile π electrons of the double bond concentrate around CCl_2 and deshield CHCl carbon, thus reducing the anisotropic effect of the π-orbitals. Chemical shift for C_2HCl_3 in a mixture of 50 vol % benzene and n-hexadecane shows only a negligible downfield excess chemical shift (15) (-0.03 ppm) (Table V-2 and Figure V-6). Dichloro-substituted carbon however indicates an upfield excess shift

of -0.18 ppm. According to the preceeding discussion this excess chemical shift indicates the existence of a preferential solvation of C_2HCl_3 by benzene.

C_2HCl_3, as solvent, induces shielding for all unsubstituted carbons in aromatic compounds (Table V-4). As it was seen before, average deviation for the unsubstituted carbons in cumene is smilar to that of benzene. Unsubstituted carbon in mesitylene shows a shielding of -0.28 ppm which is somewhat stronger, but still in the same range, as the corresponding carbons in benzene and cumene. Methyl carbon in mesitylene, however, shows a shielding of -0.57 resembling the shielding induced on β carbons in DEE and IPME. Substituted ring carbons show deshielding, very small for cumene (+0.07 ppm) and moderate for mesitylene (0.23 ppm). Those deshieldings are considerably smaller than the corresponding ones induced by $CHCl_3$ (1.16 ppm for cumene and 1.40 ppm for mesitylene). We may assume that maximum anisotropic effect induced by C_2HCl_3 is the one seen on methyl group in mesitylene, -0.57 ppm. The deshielding on Ci of cumene can then be seen as a combination of the simultaneous anisotropic shielding and an IMI induced deshielding of 0.64 ppm. Similarly the IMI induced deshielding of mesitylene may be estimated at 0.80 ppm. The ratio of those two estimated C_2HCl_3-induced deshielding effects is 0.8. This is remarkably close to the ratio of the analogous deshielding effects induced by $CHCl_3$ which is 0.829 (116:140). Both the benzene induced deviations in ^1H NMR and the comparison of the experimentally found and estimated deshielding on the substituted ring carbons suggests

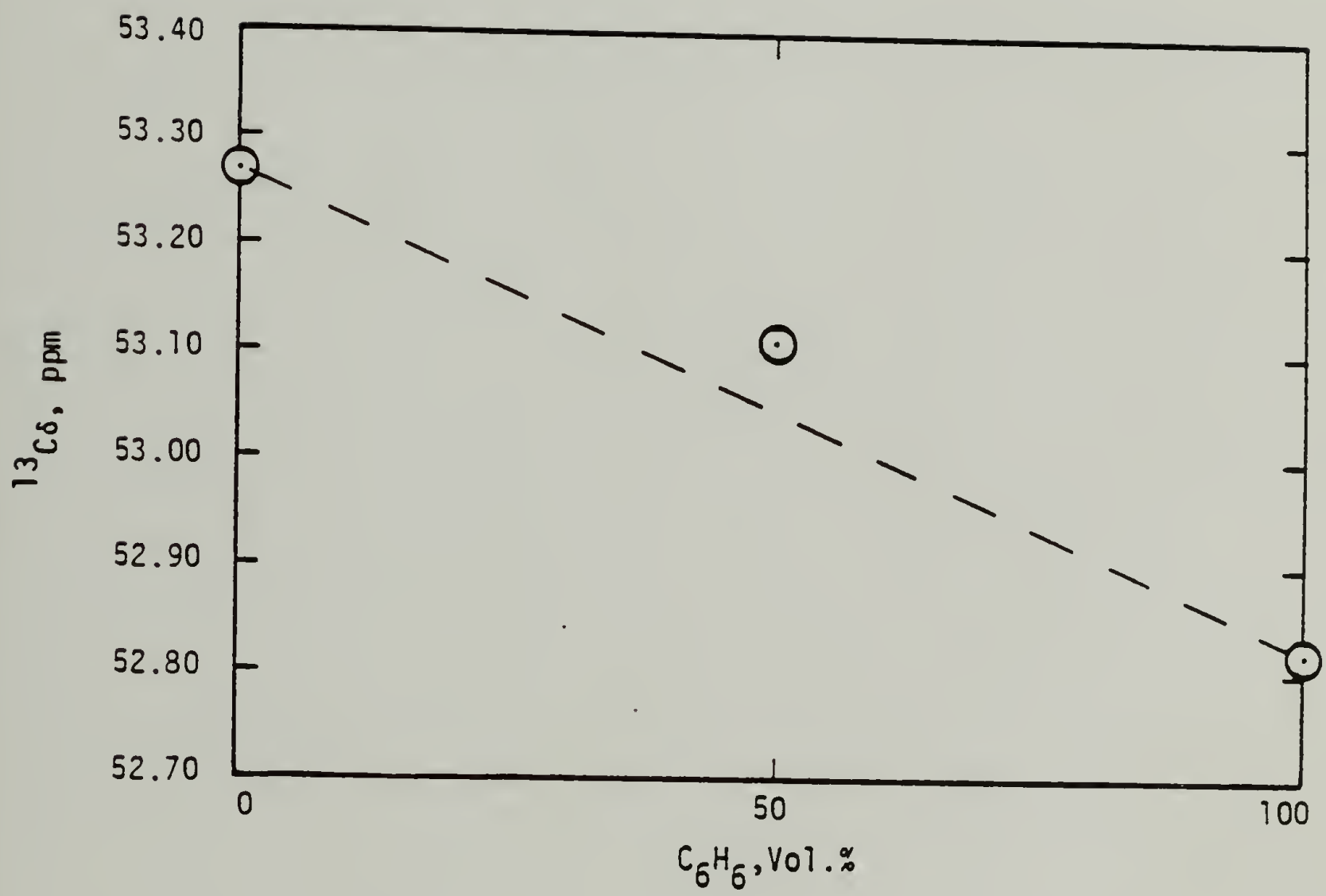
that C_2HCl_3 forms π-hydrogen bonds with aromatics which are weaker than the ones formed by $CHCl_3$. The anisotropic direction of the chemical shifts do not allow the use of the intensities of deviations to estimate the relative intensities of the IMI between C_2HCl_3 and ethers. However, based on the published results from other experiments (4,5,6) one may estimate that interaction with ethers is stronger than the one with aromatics.

Excess enthalpies of mixing of benzene and C_2Cl_4 at 30°C are reported to be moderately negative (16) moderately positive (17) or zero (4). Excess volume of mixing is strongly positive for C_2Cl_4 and benzene (18,19), slightly positive with toluene and slightly negative with p-xylene (18,19). Molar polarization increases in binary mixtures, less for benzene than for p-xylene (19). The interaction is described as a charge transfer complex (18) but UV spectrum of benzene does not show any change when benzene is codissolved with C_2Cl_4 in an inert solvent (13).

Aromatic solvents induce moderate to strong shielding of C_2Cl_4. The shielding decreases rapidly with the size of the aromatic molecule and it is apparently dependent on the steric accessibility of CCl_2 group. C_2Cl_4 dissolved in a mixture of 50 vol % of benzene in n-hexodecane shows only a negilgible excess shift (-0.02 ppm) (Table V-1 and Figure V-7) indicating the absence of the preferential solvation of C_2Cl_4 by benzene. Both of these facts suggest a van der Waals interaction.

C_2Cl_4 as a solvent induces shielding of all carbons and hydrogens

Fig. V-7. The ^{13}C NMR chemical shifts of tetrachlorethylene in mixture of n-hexadecane and benzene.


53.40
53.30
53.20
53.10
53.00
52.90
52.80
52.70
$^{13}C\delta$, ppm
0
50
100
C_6H_6, Vol.%

in aromatic solutes (Table V-5). The most noticeable is the shielding of methyl carbon in mesitylene, which is almost identical (-0.56 vs. -0.57) as the shielding induced by C_2HCl_3. It appears that this is the characteristic anisotropic deviation for an accessible nonpolar solute.

Substituted carbons of cumene and mesitylene dissolved in C_2Cl_4 shielded (-0.33 and -0.15 ppm, respectively). After subtracting the anisotropic shielding this indicates deshieldings of 0.23 ppm for cumene and 0.41 ppm for mesitylene or ~ 50%of the analogous deshielding induced by C_2HCl_3. Apparently the interaction between C_2Cl_4 and aromatic compounds is either some very weak specific or van der Waals interaction.

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C H A P T E R VI

INTERMOLECULAR INTERACTIONS OF AROMATIC COMPOUNDS

Introduction

Aromatic compounds of low molecular weight, (aromatics, in further text) are widely used as solvents for a large number of polymers (1). The understanding of the mechanism of the intermolecular interaction, IMI, involving these compounds is thus very important. One may also expect that cohesive interactions of some polymers, as polystyrene, PS, and homopolymers of alkyl-substituted styrenes are based on the mechanisms similar to these found in aromatics of low molecular weights. Similar is the case with other polymers containing aromatic groups in the chain, such as poly(2,6-dimethyl-1,4-phenylene oxide), PPO, whose specific IMI, however, have not yet been resolved. Additional reasons for the interest in the IMI of aromatic compounds is in the compatibility of PS and poly(vinyl methyl ether), PVME. This compatible blend may be obtained in nonhomogeneous form if dried from chloroform and trichloroethylene (2,3) but it is homogeneous if dried from cosolution in benzene, toluene and p-xylene. This indicates that each of those solvents has strong enough IMI to hold both of the polymers in the solution but does not prevent their mutual interaction. The mechanism of such IMI has not been analysed before.

Benzene, mesitylene, cumene and m-xylene have been selected as model compounds for this study. Mesitylene is selected because it has a large degree of alkyl substitution and should be a stronger electron

donor than benzene (4). Its methyl groups cannot hinder the access to the π-orbital but, they may, to some extent, prevent the solvent molecule from approaching a ring hydrogen while in the ring plane. Cumene, besides being a monomeric model for PS, may also demonstrate the effect of the large alkyl substituent on the IMI. The isopropyl group may be able to prevent another molecule from approaching both the ring hydrogens and the π-orbital. The m-xylene is selected primarily because it is an oxygen-free analog of the aromatic segment in PPO.

Both ^{13}C and ^{1}H chemical shifts of all model compounds, dissolved in n-alkanes,have a good linear correlation with Rummens parameter g^2 (5) (Tables VI-1 to VI-8). This is in agreement with the reported calorimetric results for the mixing of benzene and n-alkanes (6-9). This mixing is endothermic and the endothermic character is more pronounced with alkanes of higher molecular weight which indicates a very weak IMI. Although Rummens plots have been reported for ^{1}H chemical shifts of several aromatic compounds (10) the qualitative significance of the slopes of van der Waals line, Si, for such compounds has not yet been discussed. It is not yet known, at this time, whether the Si of the aromatic and nonaromatic compounds may be compared. It is noticed that in all cases Si for unsubstituted ring carbons are higher than Si for the corresponding hydrogens (Table VI-9). This relationship is similar to that seen for chloroform and trichloroethylene (See Chapters II and IV). The Si of unsubstituted ring carbons in substituted aromatics are very similar to that of benzene. The maxi-

TABLE VI-1

^{13}C NMR Chemical Shifts for Benzene in Different Solvents*

	Solvent	g^2	δcorr	δVDWL	Δ
1	C5	3.24	60.22		
2	C6	3.47	60.42		
3	C7	3.63	60.50		
4	C8	3.78	60.59		
5	C9	3.87	60.66		
6	C10	3.96	60.71		
7	C11	4.04	60.75		
8	C16	4.26	60.88	**	
9	C_6H_{12}	4.15	60.66	60.83	-0.17
10	C_6H_6	5.17	60.75	61.47	-0.72
11	CCl_4	4.62	61.45	61.12	0.33
12	$CHCl_3$	4.43	61.70	61.00	0.70
13	CH_2Cl_2	4.13	61.71	60.81	0.90
14	1,2DCE	4.43	61.85	61.00	0.85
15	1,1,1TCE	4.31	61.59	60.93	0.66
16	1,1,2,2TCE	5.08	62.48	61.41	1.07
17	1,2DBE	5.67	62.74	61.79	0.95
18	2CP	3.51	60.93	60.42	0.51
19	TBC	3.60	60.87	60.48	0.39
20	C_2HCl_3	4.84	61.04	61.26	-0.22
21	C_2HCl_3	4.84	61.04	61.26	-0.22
22	C_2Cl_4	5.24	61.04	61.52	-0.48
23	C_2Cl_4	5.24	61.05	61.52	-0.47
24	DEE	3.15	60.44	60.19	0.25
25	DEE	3.15	60.43	60.19	0.24
26	IPME	3.24	60.43	60.25	0.18
27	DIPE	3.38	60.47	60.34	0.13
28	EGDME	3.52	60.89	60.43	0.46
29	EGDME	3.52	60.86	60.43	0.46
30	DPhE	6.22	61.36	62.14	-0.78
31	C10H	2.84	60.47	59.99	0.48
32	IPrOH	3.50	60.89	60.41	0.48
33	DMSO	4.86	61.61	61.28	0.33
34	DMF	4.22	60.76	60.87	-0.11

*All values at 31°C, relative to external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (See Appendix, Table A-2). Symbols as in Appendix, Table A-1.

** Van der Waals line has the correlation 0.9968 for the equation

$$\delta = 58.19 + 63.40\ g^2 \text{ (ppm)}.$$

TABLE VI-2

^{1}H NMR Chemical Shifts for Benzene in Different Solvents*

	Solvent	g^2	δcorr	δVDWL	Δ
1	C5	3.24	3.07		
2	C6	3.42	3.11		
3	C7	3.63	3.20		
4	C8	3.78	3.26		
5	C9	3.87	3.31		
6	C10	3.96	3.36		
7	C11	4.04	3.39		
8	C16	4.26	3.46	**	
9	C_6H_6	5.17	2.91	3.84	-0.93
10	TOL	5.12	2.91	3.82	-0.91
11	CCl_4	4.62	3.79	3.61	0.18
12	$CHCl_3$	4.43	4.04	3.54	0.50
13	CH_2Cl_2	4.13	4.18	3.41	0.77
14	1,2DCE	4.43	4.15	3.54	0.61
15	1,1,2,2TCE	5.08	4.57	3.80	0.77
16	1,2,DBE	5.67	4.79	4.04	0.75
17	2CP	3.51	3.43	3.16	0.27
18	TBC	3.60	3.34	3.20	0.14
19	C_2HCl_3	4.84	3.60	3.70	-0.10
20	C_2Cl_4	5.24	3.52	3.87	-0.36
21	DEE	3.15	3.09	3.02	0.07
22	IPME	3.24	3.09	3.05	0.04
23	DIPE	3.38	3.07	3.11	0.04
24	EGDME	3.52	3.29	3.17	0.12
25	DPhE	6.22	3.25	4.27	-1.02
26	C1OH	2.84	3.10	2.89	0.21
27	IPrOH	3.50	3.43	3.16	0.27
28	DMSO	4.86	3.47	3.71	0.24
29	DMF	4.22	3.64	3.45	0.19

*All values at 37°C, relative to the external standard (10 vol % H_2O in DMSO-d_6), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

** Van der Waals line has the correlation 0.9952 for the equation:
$\delta = 1.73 + 40.70\ g^2$ (ppm).

TABLE VI-3

^{13}C NMR Chemical Shifts for Mesitylene in Different Solvents*

No	Solvent	g^2	C1,3,5			C2,4,6			$-CH_3$		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	69.22			59.01			-47.11		
2	C7	3.63	69.37			59.27			-46.71		
3	C9	3.87	69.50			59.43			-46.47		
4	C13	4.15	69.58			59.57			-46.27		
5	C16	4.26	69.67	**		59.69	**		-46.10	**	
6	C_6H_{12}	4.15	69.64	69.60	0.04	59.44	59.60	-0.16	-46.61	-46.22	-0.39
7	MES	5.13	69.60	70.02	-0.42	59.56	60.23	-0.67	-46.25	-45.29	-0.96
8	C_6H_6	5.17	69.75	70.04	-0.29	59.53	60.26	-0.73	-46.83		-1.54
9	TOL	5.12	69.74	70.02	-0.28	59.57	60.22	-0.66	-46.53	-45.24	-1.28
10	CUM	5.05	69.83	69.99	-0.16	59.69	60.18	-0.49	-46.38	-45.30	-1.08
11	CCl_4	4.62	70.13	69.81	0.32	60.13	59.90	0.23	-46.29	-45.36	-0.93
12	$CHCl_3$	4.43	71.12	69.72	1.40	60.33	59.78	0.55	-45.47	-45.78	0.31
13	CH_2Cl_2	4.13	71.05	69.60	1.45	60.18	59.59	0.59	-45.41	-45.96	0.55
14	1,2DCE	4.43	71.02	69.72	1.30	60.38	59.78	0.60	-45.72	-46.24	0.52
16	1,1,1,TCE	4.31	70.32	69.67	0.65	60.25	59.70	0.55	-45.57	-45.96	0.39
17	1,1,2,2TCE	5.08	71.85	70.00	1.85	61.15	60.20	0.95	-45.55	-46.07	0.52
18	1,2D8E	5.67	71.59	70.26	1.33	61.33	60.58	0.75	-44.60	-45.33	0.73
19	2CP	3.51	69.85	69.33	0.52	59.54	59.19	0.35	-43.99	-44.77	0.78
20	T8C	3.60	69.62	69.37	0.25	59.56	59.25	0.31	-46.48	-46.84	0.36
21	C_2HCl_3	4.84	70.13	69.90	0.23	59.77	60.05	-0.28	-46.39	-46.75	0.36
22	C_2Cl_4	5.24	69.93	70.07	0.14	59.82	60.30	-0.48	-46.13	-45.56	0.57
23	DEE	3.15	69.45	69.18	0.27	59.05	58.96	0.09	-45.74	-45.18	-0.56
24	IPME	3.24	69.46	69.22	0.24	59.11	59.01	0.10	-47.15	-47.18	0.03
25	DIPE	3.38	69.32	69.28	0.04	59.13	59.10	0.03	-47.08	-47.10	0.02
26	EGDME	3.52	69.86	69.34	0.52	59.39	59.19	0.20	-46.83	-46.96	0.13
27	C1OH	2.85	69.76	69.05	0.71	58.97	58.76	0.21	-46.94	-46.83	-0.11
28	IPrOH	3.50	69.83	69.33	0.50	59.53	59.18	0.35	-47.47	-47.47	0.00
29	DMSO	4.86	70.31	69.91	0.40	60.03	60.06	-0.03	-46.46	-46.85	0.39
30	DMF	4.22	69.76	69.64	0.12	59.21	59.65	-0.44	-45.86	-45.55	-0.31
									-47.07	-46.16	-0.91

*All values at 31°C, relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics
a) for C1,3,5 correlation 0.9946 for equation
$\delta = 67.83 + 42.82\ g^2$ (ppm)
b) for C2,4,6 correlation 0.9975 for equation
$\delta = 56.92 + 64.46\ g^2$ (ppm)
c) for $-CH_3$ correlation 0.9974 for equation
$\delta = -50.20 + 95.82\ g^2$ (ppm).

TABLE VI-4

^1H NMR Chemical Shifts for Mesitylene in Different Solvents*

No	Solvent	g^2	Ring H			CH_3		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C6	3.47	2.57			-1.98		
2	C7	3.63	2.66			-1.84		
3	C8	3.78	2.70			-1.79		
4	C9	3.81	2.73			-1.74		
5	C10	3.96	2.80			-1.71		
6	C13	4.15	2.83			-1.66		
7	C16	4.26	2.88	**		-1.60	**	
8	C_6H_{12}	4.15	2.95	2.85	-0.10	-0.84	-1.64	
9	MES	5.13	2.71	3.22	-0.51	-1.81	-1.21	-0.60
10	C_6H_6	5.17	2.43	3.23	-0.80	-2.15	-1.19	-0.96
11	CUM	5.05	2.67	3.19	-0.52	-1.89	-1.24	-0.65
12	CCl_4	4.62	3.21	3.02	0.19	-1.27	-1.43	0.16
14	$CHCl_3$	4.43	3.50	2.95	0.55	-1.07	-1.51	0.44
15	CH_2Cl_2	4.13	3.22	2.84	0.38	-0.90	-1.64	0.74
16	1,2DCE	4.43	3.94	2.95	0.99	-0.62	-1.51	0.89
17	1,1,1TCE	4.31	3.46	2.91	0.55	-1.07	-1.57	0.50
18	1,1,2,2TCE	5.08	4.01	3.20	0.81	-0.54	-1.23	0.69
19	2CP	3.51	2.87	2.60	0.27	-1.69	-1.91	0.22
20	TBC	3.60	2.86	2.64	0.22	-1.21	-1.88	0.67
21	C_2HCl_3	4.84	2.90	3.11	-0.21	-1.62	-1.34	-0.28
22	C_2Cl_4	5.24	2.95	3.26	-0.31	-1.52	-1.16	-0.36
23	DEE	3.15	2.49	2.47	0.02	-2.05	-2.07	0.02
24	IPME	3.24	2.54	2.50	0.04	-2.05	-2.03	-0.02
25	DIPE	3.38	2.49	2.55	-0.06	-2.02	-1.97	0.05
26	EGDME	3.52	2.72	2.61	0.11	-1.87	-1.91	0.04
27	C1OH	2.85	1.96	2.36	0.40	-1.02	-2.20	1.18

*All values at 37°C, relative to the external standard (10 vol % H_2O in DMSO-d6), corrected for diamagnetic susceptibility (See Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals line have the following characteristics
a) Ring H: correlation 0.9879 for the equation
$\delta = 1.28 + 37.74\ g^2$ (ppm)
b) CH_3: correlation 0.9649 for the equation
$\delta = 3.44 + 43.53\ g^2$ (ppm).

TABLE VI-5

^{13}C NMR Chemical Shift for Cumene in Different Solvents*

No	Solvent	g^2	C1			C3,5			C2,6			C4		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	80.64			60.31			58.27			57.81		
2	C6	3.47	80.76			60.46			58.42			57.96		
3	C6	3.47	80.77			60.47			58.43			57.99		
4	C7	3.63	80.76			60.50			58.46			58.00		
5	C9	3.87	80.91			60.70			58.65			58.20		
6	C10	3.96	80.94			60.72			58.67			58.23		
7	C11	4.04	81.02			60.79			58.74			58.30		
8	C12	4.11	81.02			60.84			58.79			58.33		
9	C13	4.15	80.91			60.84			58.79			58.36		
10	C16	4.26	81.00	**		60.92	**		58.87	**		58.42	**	
11	CUM	5.05	81.07	81.32	-0.25	60.92	61.38	-0.46	58.90	59.30	-0.40	58.41	58.89	-0.48
12	C_6H_6	5.17	81.10	81.36	-0.26				58.87	59.37	-0.50	58.31	58.96	-0.65
13	CCl_4	4.62	81.40	81.16	0.24	61.39	61.45	-0.06	59.39	59.06	0.33	58.90	58.63	0.27
14	$CHCl_3$	4.43	82.28	81.09	1.19	61.71	61.02	0.69	59.82	58.95	0.87	59.16	58.52	0.64
15	1,2OCE	4.43	82.37	81.09	1.28	61.76	61.02	0.74	59.88	58.95	0.93	59.22	58.52	0.70
16	1,1,2,2TCE	5.08	82.92	81.33	1.59	62.40	61.40	1.00	60.53	59.32	1.21	59.79	58.90	0.89
17	C_2HCl_3	4.84	81.36	81.24	0.12	61.05	61.26	-0.21	59.06	59.19	-0.13	58.51	58.76	-0.25
18	C_2HCl_3	4.84	81.35	81.24	0.11	61.05	61.26	-0.21	59.06	59.19	-0.13	58.51	58.76	-0.25
19	C_2Cl_4	5.24	81.12	81.38	-0.26	61.10	61.49	-0.39	59.05	59.41	-0.36	58.60	59.00	-0.40
20	DEE	3.15	80.86	80.63	0.23	60.46	60.26	0.20	58.42	58.22	0.20	57.94	57.76	0.18
21	1PME	3.24	80.62	80.66	0.16	60.48	60.31	0.17	58.47	58.28	0.19	57.95	57.82	0.13
22	1PME	3.24	80.89	80.66	0.23	60.53	60.31	0.22	58.49	58.28	0.21	57.99	57.82	0.17
23	01PE	3.38	80.69	80.71	-0.02	60.51	60.40	0.11	58.43	58.36	0.07	57.99	57.90	0.09
24	01PE	3.38	80.71	80.71	0.00	60.49	60.40	0.09	58.44	58.36	0.08	58.00	57.90	0.10
25	01PE	3.38	80.71	80.71	0.00	60.53	60.40	0.13	58.45	58.36	0.09	57.94	57.90	0.04
26	ONBE	3.79	81.01	80.86	0.15	60.77	60.64	0.13	58.72	58.59	0.13	58.25	58.14	0.11
27	EGDME	3.52	81.30	80.77	0.53	60.87	60.48	0.39	58.83	58.44	0.39	57.79	57.98	-0.19
28	p-01OX	4.09	81.70	80.97	0.77	61.18	60.81	0.37	59.23	58.76	0.47	58.65	58.32	0.33
29	OPhE	6.22	81.36	81.74	-0.38	61.20	62.07	-0.87				58.66	59.58	-0.92
30	DPhE	6.22	81.36	81.74	-0.38	61.20	62.07	-0.87	59.20	59.97	-0.77	58.66	59.58	-0.92
31	OPhM	6.18	81.33	81.72	-0.39				59.59	59.95	-0.36			
32	ANIS	5.38	81.44	81.43	0.01	61.08	61.58	-0.50	59.09	59.49	-0.40	58.50	59.08	-0.58

*All values at 31°C, relative to the external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics:
a) C1: correlation 0.9409 for the equation $\delta = 79.50 + 35.97\ g^2$ (ppm)
b) C3,5: correlation 0.9956 for the equation $\delta = 58.40 + 59.08\ g^2$ (ppm)
c) C2,6: correlation 0.9937 for the equation $\delta = 56.44 + 56.79\ g^2$ (ppm)
d) C4: correlation 0.9945 for the equation $\delta = 55.67 + 59.11\ g^2$ (ppm)

Table VI-6

^{1}H NMR Chemical Shift of Cumene in Different Solvents*

No.	Solvent	g^2	δcorr	δVDWL	Δ
1	C6	3.47	3.04		
2	C6	3.47	3.03		
3	C7	3.63	3.12		
4	C7	3.63	3.11		
5	C8	3.78	3.18		
6	C9	3.87	3.23		
7	C10	3.96	3.26		
8	C10	3.96	3.25		
9	C10	3.96	3.26		
10	C16	4.26	3.37	**	
11	C_6H_{12}	4.15	3.29	3.34	-0.05
12	ACSC6	3.52	3.10	3.07	0.03
13	ISOC8	3.69	3.18	3.14	0.04
14	CUM	5.05	3.04	3.72	-0.68
15	CUM	5.05	3.03	3.72	-0.69
16	C_6D_6	5.17	2.89	3.78	-0.89
17	CCl_4	4.62	3.68	3.54	0.14
18	$CDCl_3$	4.43	3.94	3.45	0.49
19	C_2HCl_3	5.24	3.47	3.80	-0.33
20	C_2Cl_4	4.84	3.52	3.63	-0.11
21	DEE	3.15	2.98	2.91	0.07
22	DEE	3.15	2.95	2.91	0.04
23	DIPE	3.38	2.94	3.01	-0.07
24	DIPE	3.38	2.94	3.01	-0.07
25	DIPE	3.38	2.90	3.01	-0.11
26	IPME	3.24	3.00	2.95	0.05
27	DnBE	3.79	3.40	3.18	0.22
28	EGDME	3.52	3.28	3.07	0.21
29	p-DIOX	4.09	3.48	3.31	0.17
30	DMF	4.22	2.89	3.36	-0.47

*Chemical shifts only of the single peak for all ring hydrogens. All values at 37°C, relative to the external standard (10 vol % H_2O in DMSO-d_6) corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals line has the correlation 0.9965 for the equation $\delta = 1.55 + 43.10\ g^2$ (ppm)

TABLE VI-7

^{13}C NMR Chemical Shift for 1,3-Dimethyl Benzene in Different Solvents*

No	Solvent	g^2	C1,3			C2			C5			C4,6			$-CH_3$		
			δcorr	δVOWL	Δ	δcorr	δVOWL	Δ	δcorr	δVOWL	Δ	δcorr	δVOWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	69.34			61.78			60.14			58.14			-47.02		
2	C7	3.63	69.51			62.03			60.39			58.43			-46.62		
3	C9	3.87	69.63			62.19			60.52			58.55			-46.40		
4	C14	4.19	69.75			62.39			60.72			58.76			-46.07		
5	C16	4.26	69.81			62.40			60.76			58.82			-45.99		
6	C16	4.26	69.80			62.44			60.77			58.82			-46.01		
7	C16	4.26	69.80	**		62.44	**		60.81	**		58.82	**		-46.02	**	
8	m-XYL	5.13	69.74	70.19	-0.45	62.30	62.98	-0.68	60.54	61.32	-0.78	58.58	59.39	-0.81	-46.53	-45.14	-1.39
9	C_6H_6	5.17	69.88	70.21	-0.33	62.40	63.00	-0.61	60.44	61.34	-0.90	58.57	59.41	-0.84	-46.46	-45.10	-1.39
10	CUM	5.05	69.90	70.16	-0.26	62.43	62.93	-0.50							-45.69	-45.22	-0.47
11	CCl_4	4.62	70.26	69.96	0.30	63.00	62.66	0.34	61.29	61.00	0.29	59.26	59.05	0.21	-45.32	-45.65	0.33
12	CCl_4	4.62	70.24	69.96	0.28	62.97	62.66	0.31	61.30	61.00	0.30	59.26	59.05	0.21	-45.33	-45.45	0.32
13	OEE	3.15	69.57	69.30	0.27	61.89	61.73	0.16	60.27	60.08	0.19	58.21	58.09	0.12	-46.33	-47.11	0.78
14	OIPE	3.38	69.42	69.40	0.02	61.94	61.87	0.07	60.35	60.23	0.12	58.29	58.24	0.05	-46.71	-46.88	0.17
15	DnBE	3.79	69.76	69.59	0.17	62.22	62.13	0.09	60.58	60.48	0.10	58.56	58.51	0.05	-46.49	-46.47	-0.02
16	EGDME	3.52	70.02	69.46	0.56	62.27	61.96	0.31	60.62	60.31	0.31	58.57	58.33	0.24	-46.85	-46.74	-0.11
17	p-OIOX	4.09	70.43	69.72	0.71	62.65	62.32	0.33	60.97	60.67	0.30	58.90	58.70	0.20	-46.47	-46.17	-0.30
18	OPhE	6.22	70.21	70.68	-0.47	62.73	63.67	-0.94	60.99	62.00	-1.01	58.94	60.10	-1.16	-46.03	-44.06	-1.97
19	DPhM	6.18	70.20	70.67	-0.47							58.99	60.07	-1.08	-45.98	-44.10	-1.88

*All values at 31°C, relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics: a) C1,3: correlation 0.9987 for the equation $\delta = 67.88 + 45.11\ g^2$ (ppm); b) C2: correlation 0.9985 for the equation $\delta = 59.73 + 63.39\ g^2$ (ppm); c) C5: correlation 0.9976 for the equation $\delta = 58.12 + 62.32\ g^2$ (ppm); d) C4,6: correlation 0.9988 for the equation $\delta = 56.03 + 65.41\ g^2$ (ppm); e) CH_3: correlation 0.9996 for the equation $\delta = -50.73 + 99.12\ g^2$ (ppm).

TABLE VI-8

^1H NMR Chemical Shifts for 1,3-Dimethyl Benzene in Different Solvents*

No	Solvent	g^2	C5			C4,6			C2			$-CH_3$		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C6	3.47	2.91			2.85			2.80			-1.90		
2	C7	3.63	2.99			2.90			2.86			-1.81		
3	C7	3.63	3.00			2.91			2.88			-1.82		
4	C8	3.78	3.07			2.98			2.94			-1.75		
5	C10	3.96	3.14			3.05			3.01			-1.65		
6	C10	3.96	3.15			3.07			3.03			-1.66		
7	C16	4.26	3.29	**		3.21	**		3.17	**		-1.53		
8	m-XYL	5.13	2.77	3.70	-0.93	2.69	3.60	-0.91	2.64	3.57	-0.93	-2.07	-1.11	-0.96
9	C_6D_6	5.17	2.78	3.72	-0.94	2.73	3.62	-0.89	2.64	3.59	-0.95	-2.14	-1.09	-1.05
10	C_6D_6	5.17	2.75	3.72	-0.97	2.69	3.62	-0.93	2.62	3.59	-0.97	-2.12	-1.09	-1.03
11	DIPE	3.38	2.83	2.87	-0.04	2.74	2.80	-0.06	2.69	2.75	-0.06	-1.98	-1.93	-0.05
12	DPhE	6.22												
13	DPhM	6.18	2.87	4.20	-1.33	2.79	4.09	-1.30	2.48	4.06	-1.58	-1.91	-0.62	-1.29

*All values at 37°C, relative to the external standard (10 vol % H_2O in DMSO-d_6), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics: a) C5: correlation 0.9988 for the equation $\delta = 1.27 + 47.28\ g^2$ (ppm); b) C4,6: correlation 0.9969 for the equation $\delta = 1.23 + 46.27\ g^2$ (ppm); c) C2: correlation 0.9974 for the equation $\delta = 1.18 + 46.64\ g^2$ (ppm); d) CH_3: correlation 0.9981 for the equation $\delta = -3.52 + 47.00\ g^2$ (ppm)

Table VI-9

Slopes of VDWL for Aromatic Compounds

Compound	Carbon	^{13}C			^{1}H		
		Si	%Si(C_6H_6)	Ci/CH_3	Si	%Si(C_6H_6)	$^{1}H/^{13}C$
C_6H_6		63.40	100.00		40.70	100.00	0.642
MES	Ci=Cl	42.82	67.54	0.447			
	C2	64.46	101.67		37.74	92.73	0.586
	CH_3	95.82			43.53		
CUM	Ci=Cl	35.97	56.74				
	C2	56.79	89.57				
	C3	59.08	93.19				
	C4	59.11	93.23				
	Average Unsubstituted	58.17	91.75		43.10	105.90	0.741
m-XYL	Ci=Cl,3	45.11	71.15	0.455			
	C2	63.39	99.98		46.64	114.59	0.736
	C4,6	65.41	103.17		46.27	113.69	0.707
	C5	62.32	98.30		47.28	116.17	0.759
	CH_3	99.12			47.00		
	Average Unsubstituted	64.13	101.15		46.62	114.55	0.727

mum difference is approximately a 10.5% reduction for ortho carbons in cumene, or approximately a 9% reduction for the average slope of all unsubstituted ring carbons (Table VI-9). For alkyl substituted carbons the Si are smaller than those of unsubstituted carbons in the same compound. Si for the four model compounds range from 57 to 71% of the Si for benzene.

From the reported properties of the alkyl substituted ethenes (11,12) it may be deduced that the dispersive interaction of an aromatic compound will involve the interaction between the π-orbital and the fluctuating dipole. In analogy with the sp^2 carbons in alkyl substituted ethenes (12), the Si of the substituted ring carbons may reflect only the involvement of the π-orbital in the dispersive interaction. The similarity of Si for all unsubstituted ring carbons in different alkyl substituted aromatics suggests that the interaction through the π-orbital is common to all aromatics and is, apparently, the principal mode of IMI. One may further assume that, in mesitylene, the Si for the unsubstituted carbon (64.46 ppm) reflects the two simultaneous interactions, one through π-orbital and the other through C-H bond. The interaction of the π-orbital may be expected to induce the same slope as on the substituted carbon (Si = 42.82 ppm or 66% of the total Si). The interaction of the hydrogen induces then the additional slope of 21.64 ppm (or 34%). One may expect that a simple relationship, analogous to the one between the slope of the van der Waals line and the π orbital charge densities, obtained from molecular orbital calculations, which has been reported by Cans, Tiffon

and Dubois (12) do exist also for aromatic compounds. However, any further interpretation of the results of this study would require a clearer understanding of the mechanism of the dispersive interaction than existing today.

In ^{1}H NMR Si values are considerbly different (Table VI-9). For mesitylene the shift of ring hydrogens (Table VI-6) has an Si which is 7% lower than Si of benzene. In the same time the Si is 6% higher for cumene and approximately 15% higher for m-xylene. The increased activity of the ring hydrogens in dispersive interaction may be attributed to the electron donating effect of the alkyl groups (13,14). In this case one may expect Si to change according to the Hammett (13) or Taft (14) equation. Differences between Si for hydogens in benzene and mesitylene is contrary from the expected. One apparent reason for this may be the steric hindrance. However more experimental findings are necessary before this phenomena can be fully understood.

Chemical shifts have been found for benzene, mesitylene and m-xylene dissolved in cyclohexane. For unsubstituted ring carbons small upfield deviations indicate only a dispersive interaction. This is in an agreement with the reported calorimetric and volumetric results. The mixing of aromatics and cyclohexane is weakly endothermic (15-17). This endothermic character is less pronounced in more substituted aromatics (16,18). The excess volume of mixing is positive (17,19) and it increases between 20 and 30°C (19), which indicates very weak interactions.

Cohesion energy density is found to decrease for the series of benzene, toluene, ethyl- and n-propyl-benzene (20,21). Mixing of n-heptanes with alkyl-substituted benzenes of the same series becomes less endothermic as the size of the alkyl group increases (6,7). The mixing of alkyl-substituted aromatic compounds is mildly endothermic (16,22) as is their mixing with benzene (22). It is interesting to note that the excess enthalpy of mixing depends on the difference in the degrees of alkyl substitution (16) and on the position of the substituents on the ring (16). This indicates that cohesive interaction of aromatic compounds depends on the proximity and packing of the aromatic rings. This would support the findings of Frank (23,24) and other authors (25) who from UV fluorescence spectra, concluded that aromatic molecules must be stacked parallel in order to allow the formation of the observed excimers.

A.H. Narten reported (26) that x-ray diffraction results for liquid benzene suggest a more varied arrangements of benzene molecules. He finds that the majority of the benzene molecules fit together like six-toothed bevel-gear wheels whose axes are at almost right angles. A second, small fraction should be stacked with parallel rings while a third, even smaller, fraction would have the hydrogen atoms near the ring center of another molecule (26).

NMR spectra of aromatic compounds, pure and dissolved in aromatic solvents show always, for all carbons and hydrogens moderate-to-strong upfield deviations from VDWL (Tables VI-1 to VI-8). When m-xylene is dissolved in series of mixtures with different ratios of benzene and

n-hexadecane (Table VI-10 and Figure VI-1) it shows, for all its carbons, a linear dependence of the chemical shift on the volume fraction of benzene. According to the previous reports (27,28) this indicates the absence of a preferable solvation and of any specific IMI between the m-xylene and benzene. This is in agreement with the reported endothermic mixing of benzene and alkyl substituted benzenes (22). When benzene is dissolved in a series of different concentrations of benzene in n-hexadecane (Table VI-11 and Figure VI-2) it shows an excess ^{13}C chemical shift in an upfield direction. Those chemical shifts level off after 50% of benzene. ^{1}H chemical shifts for benzene in the same series of solutions shows only a negligible, upfield excess chemical shift (Table VI-11 and Figure VI-2).

These excess chemical shifts indicate that molecules of benzene have mutually preferential solvation and suggests the existence of a specific IMI. The fact that the chemical shifts for carbon do level off, while those for hydrogen are not as much deviating from the straight line, suggests that this interaction involves primarily π-orbitals. This is in an apparent contradiction with the experimentally found intensities of deviations from VDWL for pure benzene, which are higher for proton (-0.93 ppm) than for carbon (-0.72 ppm). A further analysis is necessary, however before any resolution of this controversy can be made.

The mutual positions of mesitylene and benzene and the mode of their IMI may be understood from the chemical shifts of nuclei of mesitylene dissolved in benzene (Tables VI-3 and VI-4).

Table VI-10

^{13}C NMR Chemical Shifts for 1,3-Dimethyl Benzene in Mixtures of n-Hexadecane and Benzene

No	$\%C_6H_6$	δcorr				
		C1,3	C2	C5	C4,6	CH_3
1	0.0	69.81	62.40	60.76	58.82	-45.44
2	0.0	69.78	62.42	60.76	58.80	-46.03
3	0.0	69.80	62.44	60.77	58.82	-46.01
4	0.0	69.80	62.44	60.81	58.82	-46.02
5	9.1	69.79	62.42		58.77	-46.07
6	9.1	69.79	62.44		58.79	-46.04
7	23.1	69.81	62.42		58.75	-46.17
8	47.6		62.41		58.69	-46.25
9	47.6	69.81	62.38		58.71	-46.30
10	76.9	69.87	62.40		58.63	-43.39
11	90.1	69.86	62.37		58.59	-46.44
12	100.0	69.88	62.40	60.44	58.57	-46.46
13	100.0	69.90	62.37		58.57	-46.49

Fig. VI-1. The ^{13}C NMR chemical shifts of 1,3-dimethylbenzene in mixtures of n-hexadecane and benzene.

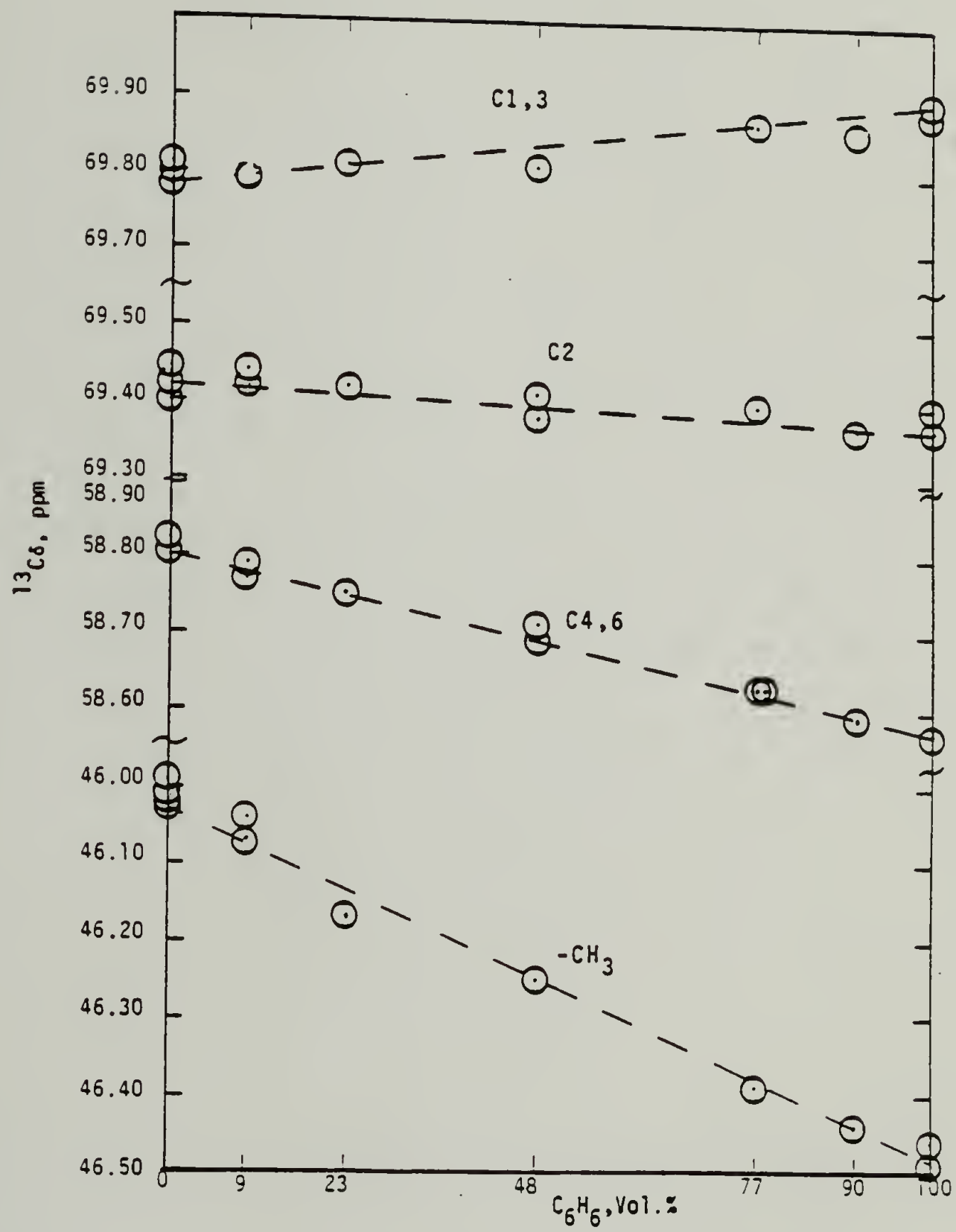
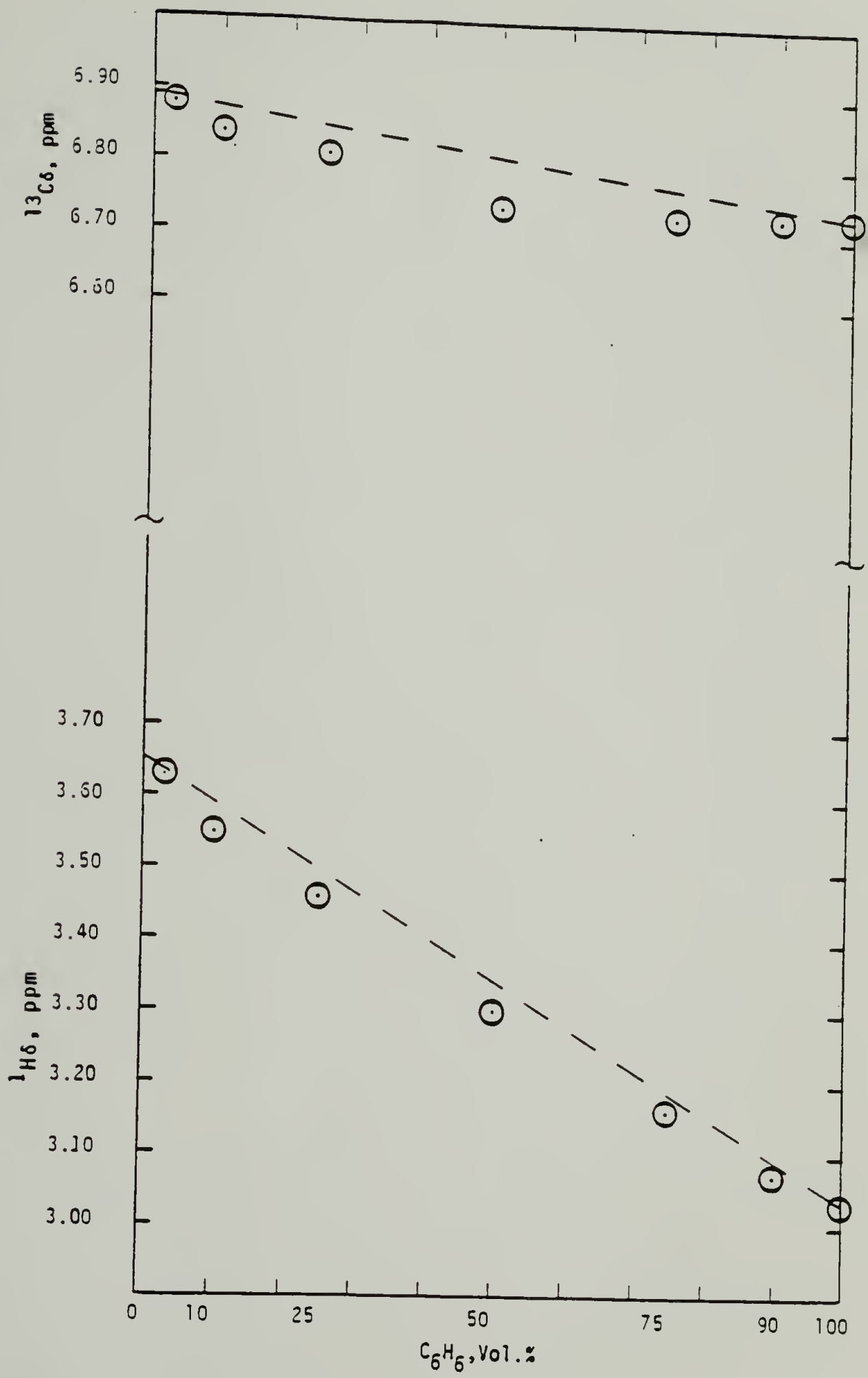

69.90
69.80
69.70
69.50
69.40
69.30
58.90
58.80
58.70
58.60
46.00
46.10
46.20
46.30
46.40
46.50
$^{13}C_\delta$, ppm
C1,3
C2
C4,6
-CH$_3$
0
9
23
48
77
90
100
C_6H_6, Vol.%

Table VI-11

^{13}C and ^{1}H NMR Chemical Shifts for Benzene in Mixtures with n-Hexadecane

No.	Vol % Benz	^{13}C δcorr	^{1}H δcorr
1	3	60.88	3.63
2	10	60.84	3.55
3	25	60.81	3.46
4	50	60.74	3.30
5	75	60.73	3.16
6	90	60.73	3.07
7	100	60.73	3.03

Fig. VI-2. The ^{13}C and ^{1}H NMR chemical shifts of benzene in mixtures with n-hexadecane.


6.90
6.80
6.70
6.60
$^{13}C\delta$, ppm
3.70
3.60
3.50
3.40
3.30
3.20
3.10
3.00
$^{1}H\delta$, ppm
0
10
25
50
75
90
100
C_6H_6, Vol.%

The methyl carbon of mesitylene is shielded -1.28 ppm, more than the most exposed methoxy group in EGDME (Chapter VII, Table VII-3).

The absence of preferential solvation indicates that there is no specific interaction between the methyl group in m-xylene and benzene. This finding may be extrapolated to methyl group of mesitylene. The carbon in this methyl group, however, is the most shielded of all carbons in mesitylene. The intensity of its shielding is also the least affected by the size of the solvent molecule (10). Apparently, this strong shielding is resulting from the multiple anisotropic effect, involving several aromatic molecules, which are surrounding the methyl group. The shielding of the corresponding hydrogen is smaller (-0.96 ppm) since it reflects the effect of only one, nearest, aromatic molecule. The shielding of the unsubstituted carbon of mesitylene has similar intensity as the shieldings of analogous carbon in m-xylene or the shielding of the carbon in benzene (-0.67, -0.77 and -0.72 ppm or the ratio 0.93:1.07:1.00, respectively). The shieldings of the three corresponding hydrogens are -0.80, -0.95 and -0.93 ppm or the ratio 0.86:1.02:1.00, respectively. The shieldings of hydrogens which are somewhat stronger than the shieldings of carbons suggest that ring hydrogens are engaged in a π-hydrogen bond. This interaction requires the benzene ring to have an average angle of 90° relative to the ring plane of the solute. A considerable reduction of the shielding, both for the carbon and for proton is seen when instead of benzene a substituted benzene is the solvent. This indicates that the two methyl groups are causing the steric hindrance. This is an additional

proof of the suggested hydrogen bond.

The substituted carbon in mesitylene is, however, shielded only -0.29 ppm. Substituted carbons of cumene and m-xylene show similar, small, benzene-induced shielding. Shielding induced by toluene and cumene are, progressively, even smaller. As it was mentioned before, the shielding of the substituted ring carbon reflects, almost exclusively, the involvement of the π-orbital in the IMI. In this case, its moderate shielding, induced by the aromatics, indicates that rings of the substituted benzene as solute and the aromatic solvent must be in the parallel position. This has already been deduced earlier for the molecules of pure benzene, and it was also mentioned by Frank (23,24) and by others (25). NMR chemical shifts however do not offer any more informations which can further explain what may be the actual mechanism the interaction among the two aromatic compounds.

Observing the deviations from VDWL for other substituted aromatic compounds one can recognize patterns identical tho those seen on mesitylene. This indicates that all the three patterns of intermolecular conformations (and interactions): clustering around the side groups, π-hydrogen bonding and parallel ring mode, exist in all cases of the interactions between aromatic compounds. In cases of pure m-xylene and mesitylene the substituted carbons are shielded approximately 50% stronger than in benzene solutions. This suggests that in the pure compounds may exist certain modes of molecular "packing" which allow parallel molecules to approach each other to a smaller distance. Another possibility is that there is a higher concentration

of the pairs of parallel molecules which may indicate some specific IMI. In either case this confirms a parallel conformation of aromatic molecules suggested by Frank (23,24). As mentioned before, the solution of m-xylene in series of benzene-n-hexadecane mixtures does not show any excess chemical shifts. This suggests that even the smallest steric hindrance prevents the preferential solvation of the two aromatic compounds. This in turn, indicates that the intensity of the IMI between the organic compounds is similar to that of the dispersive interactions.

Interaction with Ethers

Very little has been written about the interaction of aromatic compounds and ethers. LeFevre and coworkers (29) have found that the change of the Kerr constant indicate a weak interaction between dimethyl ether and benzene. The diethyl ether and benzene have a zero excess enthalpy of mixing (6). Equimolar mixing of di-n-butyl ether and benzene is, however, endothermic at 25°C. Its excess enthalpy is 500 J/mole (6). Mixing of p-dioxane and benzene in turn, shows, at temperatures between 15 and 45°C, an inversion of the excess enthalpy of mixing. The mixing is exothermic up to 75-80 vol % of p-dioxane and weakly endothermic thereafter. The endothermic character becomes less pronounced as the temperature increases. This behavior suggests that the interaction between benzene and p-dioxane is stronger than the cohesive interaction in benzene, but weaker than that in p-dioxane. When aromatic compounds are dissolved in aliphatic ethers

both their carbons and hydrogens are deshielded. As it may be seen in Tables VI-1 to VI-8 the exceptions are few.

Hydrogens at the ring of benzene, and alkyl substituted benzenes, are not strongly deshielded by aliphatic ethers (Tables VI-2, 4, 6 and 8). Ethers with higher content and more accessible oxygens, such as p-dioxane and ethylene-glycol dimethyl ether, EGDME, induce, however, a moderately strong deshielding of those hydrogens. This indicates that between the aromatic hydrogen and ether oxygen is established a weak hydrogen bond whose intensity depends on the accessibility of the latter. Ether induced deshielding of the ring carbons of the aromatic solutes is considerably stronger than that of their hydrogens (Tables VI-1, VI-3, VI-5 and VI-7). The most sensitive to the ether-induced deshielding is the carbon which is bearing an alkyl substituent. This effect is the same as the one seen for aromatic compounds dissolved in chloroform (Chapter III) or in trichloroethylene (Chapter V). This deshielding indicates that the π-orbital is engaged in the interaction with ethers. Among the ethers, the most effective in deshielding ring carbons are p-dixoane and EGDME. Deshielding by DEE and isopropyl methyl ether, IPME, is only of moderate intensity. Deshielding by DnBE is weak and by DIPE negligible. The intensities of deshielding of benzene and of substituted ring carbons of different substituted aromatics induced by the same ether are either identical or of similar intensities.

These deshieldings, induced by ethers, clearly can not be attributed to anisotropic effects. If a nucleus is to be deshielded by a

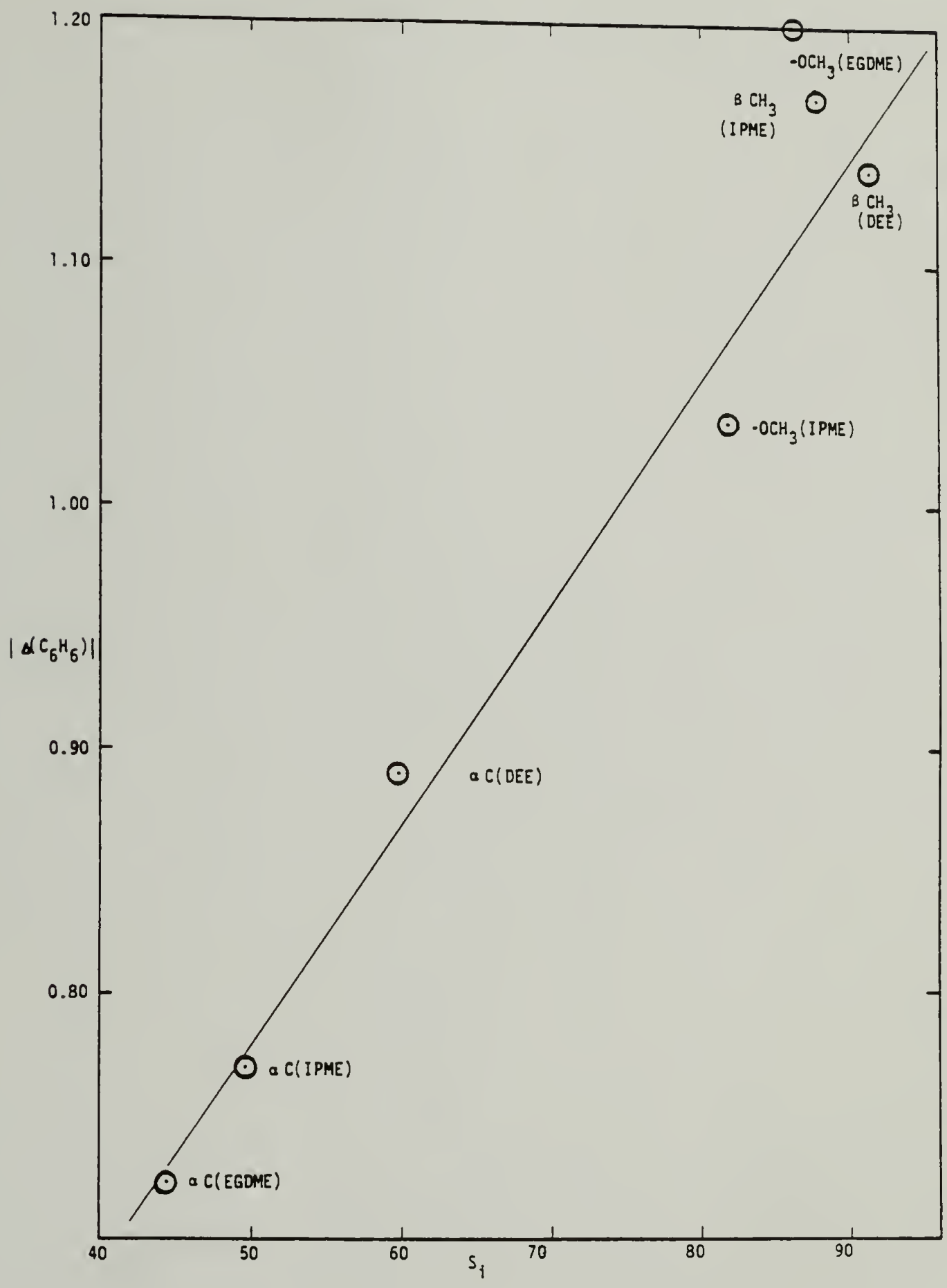
C-C or C-O bond it must be at the bond axis (31). Among all the possible positions of ethers and aromatic compounds none could be found which could cause the anisotropic shielding of the kind which is recorded experimentally. The deshieldings can not be attributed to the hydrogen bonds of ring C-H groups either. If the recorded deshielding of the ring carbons were from the hydrogen bond a corresponding strong deshielding would have to be seen also for their corresponding hydrogens, which is not the case. An aromatic solvent induces usually anisotropic shielding of the solute. The intensity of this shielding may depend on either one or both, the distance betwen the π-orbital and the observed nucleus (10) and the intensity of the IMI. Intensities of benzene-induced shieldings for polarized solutes have already been analysed in Chapters III and V and also by other authors (32-34). For substituted benzenes they depend on the polarization of C-H bond (32,33). For methoxy benzene (anisole) the differences of chemical shifts in CCl_4 and benzene are reportedly proportional to the parameters of Hammet equation (34). All carbons of DEE, EGDME and IPME dissolved in benzene, m-xylene and mesitylene show anisotropic shieldings which are approximately 100% stronger than the reported corresponding shielding on carbons of neononane, $C(CH_2CH_3)_4$, (10). When IPME is dissolved in mixture of 50 vol % of benzene and n-hexadecane all of its three carbons show a small upfield excess chemical shift (Table VI-12 and Figure VI-3). Both of those results suggest that polarized C-H bonds in ethers form specific IMI with aromatics (27). Since ethers induce deshielding of the substituted car-

Table VI-12

^{13}C NMR Chemical Shifts for Isopropyl Methyl Ether in Mixtures of Benzene and n-Hexadecane

No.	% C_6H_6	δcorr		
		αCH	OCH_3	βCH_3
1	0	5.26	-12.02	-45.55
2	50	5.06	-12.22	-45.80
3	100	4.94	-12.29	-45.91

Fig. VI-3. Correlation between benzene-induced deviation from van der Waals line and the slope of this line for carbons in some ethers.


1.20
1.10
1.00
0.90
0.80
| α(C6H6) |
-OCH3(EGDME)
β CH3 (IPME)
β CH3 (DEE)
-OCH3(IPME)
α C(DEE)
α C(IPME)
α C(EGDME)
40
50
60
70
80
90
Si

bons in aromatics, indicating the engagement of the π-orbital this IMI is probably a π-hydrogen bond engaging electron deficient hydrogens in the ether. However, benzene induced deviations from VDWL, Δδ, for all carbons in the three ethers, which were mentioned before, show a remarkably good linear correlation with their respective Si values (Table VI-13 and Figure VI-4). This suggests that, even if the interaction may be stronger than dispersive, most of the shielding is purely anisotropic in nature. It depends primarily on the steric accessibility of the structural group containing the observed carbon. The intensity of the IMI between an ether and an aromatic should depend on the electron-donating power of the latter. In the case of the alkyl-substituted aromatics, however, the electron donating power should rise with the concentration or size of the alkyl substituents (4,13,14). Substituents, on the other side, increase the minimal distance to which a solvent molecule can approach the polarized C-H bond of the solute. This reduces the possible anisotropic effect (10).

All three of ethers which were analysed as solutes, DEE, IPME and EGDME show anisotropic shieldings of all their nuclei when dissolved in aromatic solvents. The intensity of the shielding varies from solvent to solvent but the pattern of those changes is different for different carbons (Tables VII-1 to VII-3).

For the methoxy group in IPME the intensity of the aromatic SIS changes in the order o-XYL = m-XYL > p-XYL > MES > TOL > C_6H_6 > CUM > DIPB (Table VII-1). The deviation from VDWL induced by mesitylene is

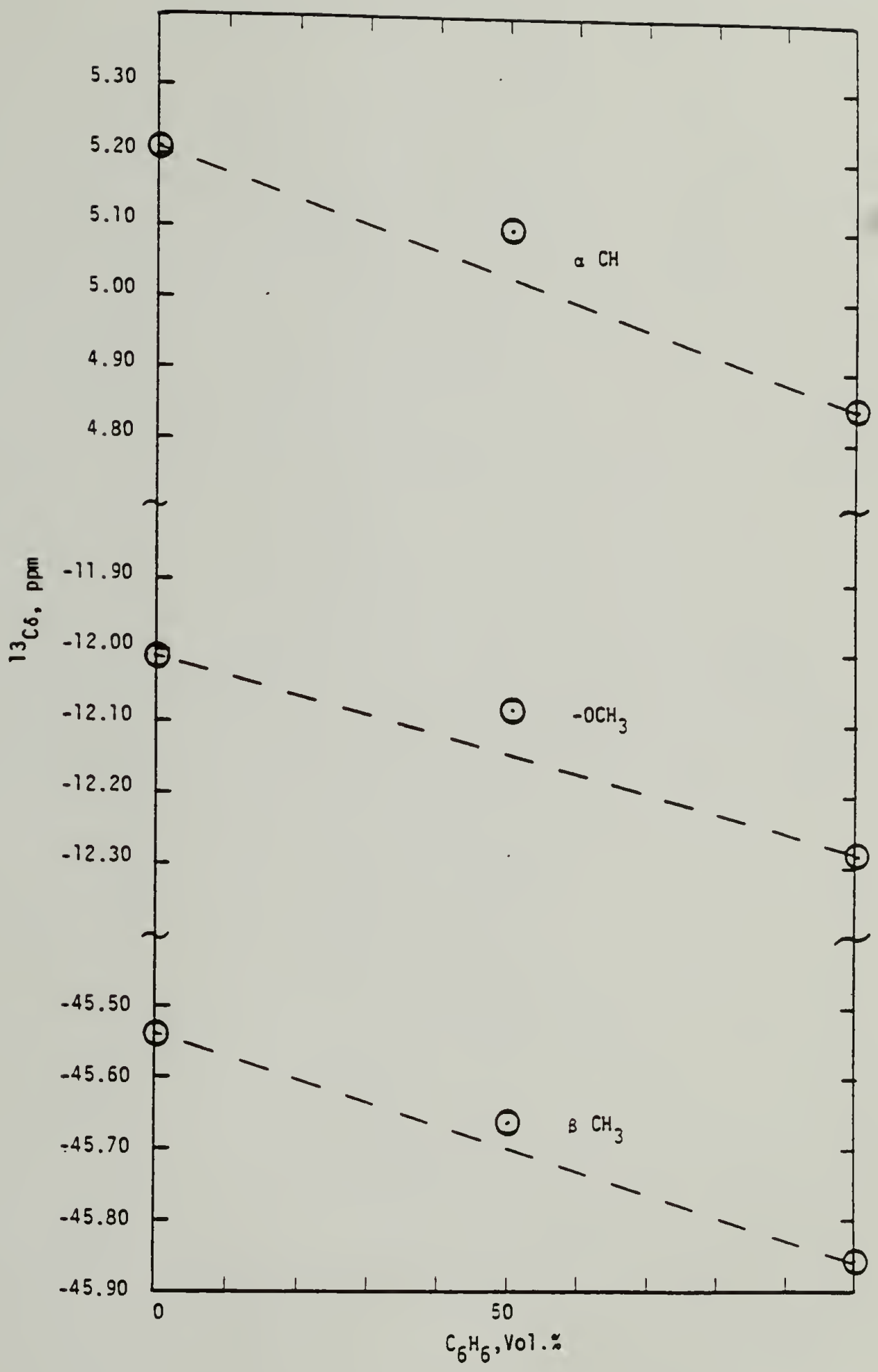
Table VI-13

Relation Between Benzene-Induced Deviation from VDWL, Δ_B, and the Slope of VDWL for Different Ethers

No.	Ether	Carbon	Si	$\lvert \Delta_B \rvert$
1	EGDME	αC	44.41	0.72
2	IPME	αC	49.63	0.77
3	DEE	αC	59.67	0.89
4	IPME	OCH_3	81.83	1.03
5	EGDME	OCH_3	86.19	1.20
6	IPME	βCH_3	87.88	1.17
7	DEE	βCH_3	91.10	1.14

The straight line has the correlation 0.9876 for the equation $\lvert \Delta_B \rvert = 0.3185 + 0.0092$ Si

Fig. VI-4. The ^{13}C NMR chemical shifts for isopropyl methyl ether in mixtures of n-hexadecane and benzene.


5.30
5.20
5.10
5.00
4.90
4.80
α CH
-11.90
-12.00
-12.10
-12.20
-12.30
-OCH3
-45.50
-45.60
-45.70
-45.80
-45.90
β CH3
13Cδ, ppm
0
50
C6H6, Vol.%

1.09 times stronger than that induced by benzene. An opposite example is α carbon in IPME for which the deviations change in order C_6H_6 > TOL > p-XYL > m-XYL > MES > o-XYL > CUM > DIPB. In this case the deviation induced by mesitylene is only 77% of that induced by benzene. Apparently, methoxy group in IPME is not excessively hindered for the approach of substituted aromatic compounds. Thus the electron donating ability of the latter plays the major role in forming IMI. The α C-H bond is polarized to the similar extent as the one in the carboxy group but it is less accesible. It does show the largest anisotropic effect induced by the aromatic solvent with the smallest molecule. Similar relations are seen for other carbons of those ethers which were analysed as solutes (Tables VII-1 to VII-3).

A few cases have been seen where ethers as solvents induce shielding of some ring carbons in the alkyl-substituted aromatics. The reason for this are the diamagnetic anisotropies of C-C and C-O bonds, which induce shielding of nuclei aside from the bond axis (31). The EGDME induces a moderate shielding of the para carbon in cumene. The very existence of this shielding and its position implies that the methoxy group of EGDME is interacting with the π-orbital thus "anchoring" the molecule of EGDME to the ring. Since the isopropyl group hinders the access to the π-orbital from the direction of the substituted and ortho carbons the EGDME has a preferred position "away" from the substituent. This position exposes para carbon to the strongest shielding of the C-O bond. Mesitylene dissolved in DIPE shows weak shieldings of both its ring and methyl hydrogens. The DEE and IPME

both induce negligible shieldings of its methyl hydrogen. All those shieldings indicate that every ether has a π-hydrogen bond with mesitylene. The shielding is then induced by the C-C or C-O bonds which are removed from the C-H bond involved in the IMI. Since benzene is a quadripole (35) one may consider the possibility that its interaction with ether is a dipole-quadripole interaction (36). As a quadripole, benzene may be interacting in two ways. In one, its electron negative sections, with high concentration of π-electrons, would attract positive ends of the ether alkyl segments. In this mode of interaction the chemical shift of ether would change upfield and that of the aromatics downfield (31,37). In the second, the electropositive section of the benzene quadripole, its ring hydrogens, would interact with the oxygen of the ether. This interaction would induce deshielding of the ring hydrogen and a smaller deshielding of the ring carbon. Both of those estimated changes may be accommodated with our experimental findings. However, the second mode of interaction would induce a very strong anisotropic deshielding on the carbons in ether, the strongest being for α carbons (31). This is opposite to our experimental results. In addition those two kinds of interactions cannot explain the similar intensities of ether-induced deshieldings for different aromatic compounds, the difference in deshieldings on different carbons in the same aromatic compound and the existence of the anisotropic shieldings on some of the nuclei in the aromatic compound. If benzene interacts as quadripole its interaction with p-dioxane would be a quadripole-quadripole interaction (36). This can-

not be accommodated with moderate deshielding of all ring hydrogens. It also does not agree with the fact that, among all ethers, which were analyzed, p-dioxane induces the strongest deshielding of the ring carbons. From all this it may be concluded that the dipole (ether)-quadripole (benzene) interaction does not make any significant contribution to the energy of IMI between ethers and aromatic compounds.

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C H A P T E R VII

INTERMOLECULAR INTERACTIONS OF ETHERS

Introduction

The aim of this study is to further the understanding of the intermolecular interactions, IMI, of poly(vinyl methyl ether), PVME. To this end it is necessary to evaluate typical IMI established by its structural segments: methoxy, α methyne and β methylene groups. Three aliphatic ethers of low molecular weight have been selected as model compounds. Isopropyl methyl ether, IPME, is a monomeric model for PVME, with the methoxy and α methyne group. Ethylene glycol dimethyl ether, EGDME, is a compound with two methoxy groups, having no steric hindrance within the molecule. It may serve as the model for the maximally acessible methoxy groups. Diethyl ether, DEE, has two ethoxy groups, which are also without steric hindrance within the molecule. Their IMI may be compared with those of methoxy group under the identical conditions. This comparison may elucidate the effect of the alkoxy group size and of the C-H bond-oxygen distance on the IMI.

Interactions of ethers with other compounds of interest have been analysed in Chapters III to VI. The analysis presented here has been made in order to understand the cohesive interaction of the pure ethers and their interactions with other ethers. This analysis is of interest both in order to understand the cohesive interactions of PVME and because very little has been published about the ether-ether interactions.

Mixing of different aliphatic ethers with n-alkanes is mildly endothermic (1) indicating the absence of any specific IMI between the two kinds of compounds. Chemical shifts of all carbons of the three ethers analysed in this work show, in Rummens plot, an excellent correlation with g^2 (Tables VII-1 to VII-3).

The slope of VDWL for β carbon in DEE is 91.10 ppm. This value has the same order of magnitude as Si for CH_3 carbons in mesitylene (Table VI-3), m-xylene (Table VI-7), acetone (4), trimethyl ethene (6) and tetramethyl ethene (5). It is, however, larger than Si for $-CH_3$ carbon in n-pentane (70.50) (7). This indicates that βCH_3 in DEE is a group whose accessibility for n-alkanes is unaffected by an intramolecular steric hindrance. This is in an agreement with the conclusion of Bent (8) that α hydrogens in ethers maintain position trans from the free electron pairs of oxygen. This conformation makes DEE a stiff molecule of a crescent shape. The access to its CH_3 groups is thus completely unhindered. The Si for α carbon is almost 35% smaller. Since α C-H groups are polarized, and they are at opposite sides of the free electron pairs of the oxygen the only apparent explanation for this lower value of Si is the crowding of α hydrogens. All four α hydrogens are in one plane and if one of them is involved in the interaction with one molecule of n-alkane the access to the other three is considerably hindered. Any molecule interacting with βCH_3 also reduces the access to α hydrogen. In addition such mutual exclusion of the molecules of solvent may be expected to be more pronounced for alkanes of higher molecular weight, thus bringing a further reduction of Si.

Table VII-1

^{13}C NMR Chemical Shifts for Isopropylmethylether in Different Solvents*

No	Solvent	g^2	αC			OCH_3			βCH3		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	4.74			-12.85			-46.45		
2	C6	3.47	4.90			-12.62			-46.20		
3	C7	3.63	4.94			-12.56			-46.13		
4	C8	3.78	5.02			-12.40			-45.95		
5	C9	3.87	5.07			-12.33			-45.88		
6	C10	3.96	5.10			-12.25			-45.80		
7	C11	4.04	5.17			-12.19			-45.74		
8	C12	4.11	5.19			-12.13			-45.67		
9	C13	4.15	5.20			-12.08			-45.63		
10	C16	4.26	5.26	**		-12.02	**		-45.55	**	
11	C_6H_{12}	4.15	5.13	5.21	-0.08	-12.29	-12.10	-0.19	-45.97	-45.64	-0.33
12	IPME	3.24	4.77			-12.75	-12.84	0.09	-46.38	-46.44	0.06
13	DEE	3.15	4.73	4.71	0.02	-12.80	-12.92	0.12	-46.44	-46.52	0.08
14	DIPE	3.38	4.67	4.83	-0.16	-12.59	-12.73	0.14	-46.28	-46.31	0.03
15	DnBE	3.79	5.07	5.03	0.04	-12.36	-12.39	0.03	-45.94	-45.95	0.01
16	EGDME	3.52	5.01	4.89	0.12	-12.55	-12.61	0.06	-46.14	-46.19	0.05
17	p-OIOX	4.09	5.25	5.18	0.07	-12.32	-12.15	-0.17	-45.91	-45.69	-0.22
18	CCl_4	4.62	5.68	5.44	0.24	-11.44	-11.71	0.27	-44.93	-45.22	0.29
19	$CHCl_3$	4.43	6.23	5.35	0.88	-10.95	-11.87	0.92	-44.89	-45.40	0.51
20	CH_2Cl_2	4.13	5.98	5.20	0.78	-11.19	-12.11	0.92	-45.08	-45.65	0.57
21	1,2DCE	4.43	6.14	5.35	0.79	-11.18	-11.87	0.69	-44.92	-45.39	0.47
22	1,1,1,TCE	4.31	5.75	5.29	0.46	-11.38	-11.98	0.60	-44.87	-45.50	0.63
23	1,1,2,2TCE	5.08	6.63	5.67	0.96	-10.29	-11.34	0.05	-44.17	-44.82	0.65
24	DCP	3.51	5.16	4.89	0.27	-12.86	-12.62	-0.24	-45.75	-46.20	0.45
25	TBC	3.60	5.02	4.93	0.09	-12.15	-12.55	0.40	-45.65	-46.12	0.47
26	C_2HCl_3	4.84	5.54	5.55	-0.01	-11.99	-11.53	-0.46	-45.62	-45.03	-0.59
27	C_2Cl_4	5.24	5.49	5.75	-0.26	-11.69	-11.21	-0.48	-45.33	-44.68	-0.65
28	C_6H_6	5.17	4.94	5.71	-0.77	-12.29	-11.26	-1.03	-45.91	-44.74	-1.17
29	TOL	5.12	4.94	5.69	-0.75	-12.38	-11.30	-1.08	-45.92	-44.78	-1.14
30	CUM	5.05	5.15	5.65	-0.50	-12.17	-11.36	-0.81	-45.71	-44.85	-0.86
31	MES	5.13	5.10	5.69	-0.59	-12.42	-11.30	-1.12	-45.92	-44.78	-1.14
32	o-XYL	5.23	5.27	5.74	-0.47	-12.36	-11.21	-1.15	-45.98	-44.69	-1.29
33	m-XYL	5.13	5.02	5.69	-0.67	-12.45	-11.30	-1.15	-45.99	-44.78	-1.21
34	p-XYL	5.10	4.96	5.68	-0.72	-12.45	-11.32	-1.13	-45.99	-44.80	-1.19
35	OIPB	5.02	5.12	5.64	-0.52	-12.11	-11.39	-0.72	-45.57	-44.87	-0.70
36	C1OH	2.85	5.53	4.56	0.97	-12.85	-13.17	0.32	-46.87	-46.78	0.09

*All values at 31°C, relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics: a) for αC correlation 0.9960 for the equation $\delta = 3.15 + 49.63\ g^2$ (ppm); b) for OCH_3 correlation 0.9982 for the equation $\delta = -15.49 + 81.83\ g^2$ (ppm); c) for CH_3 correlation 0.9984 for the equation $\delta = -49.28 + 87.88\ g^2$ (ppm).

Table VII-2

^{13}C NMR Chemical Shifts for Diethyl Ether in Different Solvents*

No	Solvent	g^2	αCH_2			βCH_3		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	-2.16			-52.86		
2	C7	3.63	-1.93			-52.52		
3	C8	3.78	-1.85			-52.39		
4	C9	3.87	-1.80			-52.29		
5	C10	3.96	-1.73			-52.22		
6	C16	4.26	-1.55	**		-51.93	**	
7	C_6H_{12}	4.15	-1.52	-1.62	0.10	-51.63	-52.04	-0.41
8	DEE	3.15	-2.20	-2.22	0.02	-52.89	-52.95	0.05
9	DEE	3.15	-2.20	-2.22	0.02	-52.89	-52.95	0.05
10	DIPE	3.38	-2.20	-2.08	-0.12	-52.62	-52.74	0.12
11	DnBE	3.79	-1.83	-1.84	0.01	-52.35	-52.37	0.02
12	EGDME	3.52	-1.97	-2.00	0.03	-52.59	-52.61	0.02
13	p-DIOX	4.09	-1.71	-1.66	-0.05	-52.24	-52.10	-0.14
14	CCl_4	4.62	-1.19	-1.34	0.15	-51.36	-51.61	0.25
15	CCl_4	4.43	-0.69	-1.45	0.76	-51.30	-51.79	0.49
16	CH_2Cl_2	4.13	-0.89	-1.63	0.74	-51.47	-52.06	0.59
17	1,2DCE	4.43	-0.88	-1.45	0.57	-51.26	-51.79	0.53
18	1,1,1,TCE	4.31	-1.41	-1.53	0.12	-52.05	-51.89	0.16
19	1,1,2,2TCE	5.08	-0.26	-1.07	0.81	-50.54	-51.19	0.65
20	2CP	3.51	-1.80	-2.00	0.20	-52.21	-52.62	0.41
21	TBC	3.60	-1.92	-1.95	0.03	-52.11	-52.54	0.43
22	C_2HCl_3	4.84	-1.51	-1.21	-0.30	-52.06	-51.41	-0.65
23	C_2Cl_4	5.24	-1.36	-0.97	-0.39	-51.69	-51.05	-0.64
24	C_6H_6	5.17	-1.90	-1.01	-0.89	-52.25	-51.11	-1.14
25	TOL	5.12	-1.92	-1.04	-0.88	-52.27	-51.16	-1.11
26	CUM	5.05	-1.73	-1.08	-0.65	-52.08	-51.22	-0.86
27	MES	5.13	-1.82	-1.04	-0.78	-52.21	-51.15	-1.06
28	o-XYL	5.23	-1.75	-0.98	-0.77	-52.29	-51.06	-1.23
29	m-XYL	5.13	-1.91	-1.04	-0.87	-52.32	-51.15	-1.17
30	p-XYL	5.10	-1.95	-1.06	-0.89	-52.29	-51.17	-1.12
31	DIPB	5.02	-1.67	-1.10	-0.57	-51.96	-51.25	-0.71
32	C1OH	2.85	-1.93	-2.40	0.47	-53.34	-53.22	-0.12

*All values at 31°C, relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics: a) for αC, correlation 0.9935 for the equation $\delta = -4.10 + 59.62\ g^2$ (ppm); b) for βC, correlation 0.9995 for the equation $\delta = -55.82 + 91.10\ g^2$ (ppm)

Table VII-3

^{13}C NMR Chemical Shifts for Ethylene Glycol Dimethyl Ether in Different Solvents*

No	Solvent	g^2	CH_2			OCH_3		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	4.43			-9.58		
2	C7	3.63	4.65			-9.21		
3	C7	3.63	4.65			-9.23		
4	C8	3.78	4.70			-9.15		
5	C9	3.87	4.78			-9.02		
6	C10	3.96	4.81			-8.96		
7	C16	4.26	4.87	**		-8.69	**	
8	EGDME	3.52	4.46	4.00	-0.13	-9.37	-9.33	-0.04
9	DIPE	3.38	4.38	4.53	-0.15	-9.33	-9.45	0.12
10	DnBE	3.79	4.67	4.71	-0.04	-9.08	-9.10	0.02
11	p-DIOX	4.09	4.56	4.84	-0.28	-9.10	-8.84	-0.26
12	CCl_4	4.62	5.11	5.08	0.03	-8.10	-8.38	0.28
13	$CHCl_3$	4.43	5.28	4.99	0.29	-7.49	-8.55	1.06
14	CH_2Cl_2	4.13	5.25	4.86	0.39	-7.97	-8.81	0.84
15	1,2DCE	4.43	5.31	4.99	0.32	-8.01	-8.55	0.54
16	1,1,1,TCE	4.31	5.17	4.94	0.23	-8.12	-8.65	0.54
17	1,1,2,2TCE	5.08	5.71	5.28	0.43	-7.02	-7.99	0.97
18	2CP	3.51	4.67	4.58	0.09	-8.94	-9.43	0.40
19	TBC	3.60	4.57	4.62	-0.05	-9.85	-9.26	0.31
20	C_2HCl_3	4.84	4.70	5.18	-0.48	-8.73	-8.20	-0.53
21	C_2Cl_4	5.24	4.96	5.35	-0.39	-8.37	-7.85	-0.52
22	C_6H_6	5.17	4.45	5.32	-0.72	-9.11	-7.91	-1.20
23	TOL	5.12	4.46	5.30	-0.84	-9.06	-7.95	-1.11
24	CUM	5.05	4.65	5.27	-0.62	-8.91	-8.01	-0.90
25	MES	5.13	4.57	5.06	-0.73	-9.18	-7.95	-1.23
26	o-XYL	5.23	4.46	5.35	-0.84	-9.12	-7.86	-1.26
27	m-XYL	5.13	4.44	5.30	-0.86	-9.23	-7.95	-1.28
28	p-XYL	5.10	4.44	5.29	-0.85	-9.25	-7.97	-1.28
29	DIPB	5.02	4.77	5.25	-0.49	-8.88	-8.04	-0.84
30	C1OH	2.85	3.96	4.29	-0.32	-9.74	-9.91	0.18

*All values at 31°C, relative to the external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following characteristics: a) for CH_2, correlation 0.9770 for the equation $\delta = 3.03 + 44.41\ g^2$ (ppm); b) for OCH_3, correlation 0.9969 for the equation $\delta = -12.37 + 86.19\ g^2$ (ppm).

Pure DEE shows only a negligible deshielding of its α carbon (0.02 ppm) and a very small deshielding of the β carbon (0.08 ppm). An analysis of the model indicates that α hydrogen cannot approach oxygen of another DEE molecule without causing the overlaps of β methyl groups. This explains the absence of any specific interaction. The small deshielding of βCH_3 indicates that a weak hydrogen bond exists between its β hydrogen and oxygen. This seems inconsistent with the extremely low boiling point of DEE (34.6° C compared with 36°C for n-pentane), but it is reflected in the cohesive energy density which is 54.76 cal/cm^3 for DEE and 49.70 cal/cm^3 for n-pentane (9). The IPME shows high slope of the VDWL for βCH_3 (87.88 ppm) which is of the same order of magnitude as for the β carbon in DEE, indicating its high accessibility. The Si for methoxy carbon is also high (81.83 ppm) and its small decrease relative to β carbon may be attributed to their steric effect. As discussed in the case of DEE the small Si value for α carbon may be explained by the crowding of n-alkane molecules interacting with both methoxy and βCH_3 groups, which prevent access to α hydrogen.

Pure IPME shows only a very weak deshielding of methoxy and β carbons (0.09 nd 0.06 ppm respectively) and no deviation at all on the α carbon. Apparently methoxy groups can form a weak hydrogen bond with oxygen in another IPME molecule. A similar but reduced tendency exists for β hydrogen too. The α hydrogen cannot form a hydrogen bond with the oxygen in IPME because of the mutual hindrance of βCH_3 and methoxy groups of the two molecules. Those weak hydrogen bonds do

show, however, a small contribution in raising the boiling point of IPME (34°C) above that of its nonpolar analog, 2-methyl butane (30°C). Slopes of VDWL of carbons in EGDME are 86.19 for the accessible methoxy group but only 44.41 ppm for the α carbon, whose hydrogen may be less accessible because of the alkane molecules already interacting with the methoxy group.

Pure EGDME shows a small shielding of its α carbon (-0.13 ppm) and a negligible shielding of the methoxy carbon (-0.04 ppm). It may be assumed that the molecule of EGDME has its lowest potential energy when the two αCH_2 groups are in trans conformation. In this conformation the two CH_2-O bonds are parallel but oriented in the opposite direction. The same happens with the two O-CH_3 bonds in the molecule. If a hydrogen bond is formed between a methoxy group in one EGDME molecule and the oxygen in the other, the C-O bond of the proton donor will have an anisotropic effect on the carbon in the methoxy group and on the carbons α and β to the oxygen in the electron donor. Methoxy grop which is under the anisotropic effect may however, be engaged in a hydrogen bond causing deshielding, so the cumulative effect is only a negligible deviation. If α hydrogen were to form the hydrogen bond with another molecule of EGDME the two molecules would have to be in parallel planes and the filled orbital of the oxygen and αC-H bond would have to be colinear. The steric hindrance would restrict any motion of the molecules to a rotation within those two planes. Clearly this mutual position of the molecules appears to be too restrictive and an engagement of α hydrogen in the hydrogen bond does

not appear probable. This absence of the hydrogen bond and of the related deshielding is an apparent reason that the α carbons reflect only the anisotropic shielding. The hydrogen bonds engaging methoxy groups may explain the difference in boiling points of EGDME (85°C) and n-hexane (68°C).

Interactions Between Different Ethers

In the few reported cases the mixing of different ethers is endothermic (1,2) indicating that the IMI between the two different ethers must be weak. DEE dissolved in di-n-butyl ether, DnBE, and in EGDME (Table VII-1) shows only negligible deviations on both carbons. For DnBE this may be understood as the indication of only dispersive interaction. The same explanation does not appear plausible for EGDME. If EGDME interact with DEE as a proton donor, both α and β carbon of the latter will be exposed to the anisotropic shielding of the O-C bond. Similarly, if either α or β hydrogen of DEE is engaged in the hydrogen bond with EGDME the neighboring carbon would be exposed to the anisotropic effect. Chemical shifts of EGDME dissolved in DEE are not available nor are any calorimetric results for the mixture of the two ethers. It appears probable, however, that they form hydrogen bonds.

When DEE is dissolved in diisopropyl ether, DIPE, its β carbons show a weak deshielding (0.12 ppm) indicating a weak hydrogen bond. The α carbon shows a weak shielding (-0.12 ppm) which may be attri-

buted to the anisotropic shielding by the isopropoxy group. In p-dioxone DEE shows shielding,-0.05 ppm for α and -0.14 ppm for β carbon. A possible explanation for this is that p-dioxane forms a hydrogen bond as proton donor with the oxygen of DEE. In such an interaction the anisotropic effect of C-O will be more visible on the β than on the α carbon. The oxygens of other p-dioxane molecules may approach hydrogens in DEE, so one may expect the hydrogen bonds in which DEE is a proton donor. Apparently the recorded deviation is the sum of the several simultaneous effects.

When IPME is dissolved in DEE it shows a weak deshielding of its methoxy and β methyl and a negligible deshielding of its α carbon. The distribution of the intensities of deshielding is the same as in pure IPME. This suggests that the mode of the interaction is the same too, engaging the methoxy group in a weak, and β methyl group in an even weaker hydrogen bond with the oxygen in DEE. The intensities of the deshieldings are approximately 25% higher than in pure IPME which probably reflects the increased accessibility of the oxygen in DEE as compared to IPME. As it does for DEE, DnBE acts as a van der Waals solvent for IPME too, inducing only negligible deviations.

The effect of DIPE on IPME is similar to that which it has on DEE. Methoxy carbon is deshielded, indicating the hydrogen bond, α hydrogen is shielded reflecting the anisotropic effect of the isopropoxy group while removed βCH_3 shows only a negligible deviation. This distribution of the DIPE-induced deviations agrees with the assumed most favorable conformation of IPME which has βCH_3 at the farthest position

from the methoxy CH_3 group. With p-dioxane IPME apparently interacts as an electron donor, similar to the case of DEE. In this interaction both methoxy and β carbons are exposed to the anisotropic effect of the C-O bond. The α carbon is sheltered by the oxygen of IPME and it does not show the anisotropic shielding. As in the case of DEE it may be assumed that hydrogens in IPME also enter in hydrogen bonds with the oxygen of p-dioxane, and the deshielding of α carbon confirms this. EGDME induces a weak deshielding of α carbon in IPME and negligible deshielding of other carbons. It does not appear possible that α hydrogens are favored for the interaction with the oxygen of EGDME over the hydrogen in the methoxy group. One probable explanation for the recorded deviations may be that IPME interacts with EGDME as an electron donor. When the methoxy group of EGDME is attached to the oxygen of IPME the anisotropic effect of its C-O bond induces the shielding which can neutralize the deshielding of the hydrogen-bonded methoxy and βCH_3 group. As in the p-dioxane solution, α carbon is sheltered from the anisotropic effect and shows only the deshielding.

When EGDME is dissolved in ethers deviations indicate the effects already seen in the case of DEE and IPME. DnBE acts as a van der Waals solvent inducing only negligible deviations. DIPE interacts as electron donor with the most accessible polarized C-H bond and induces the anisotropic shielding on the α carbon. P-dioxane induces the shielding of carbons near the oxygen. In this case, since both carbons are in a similar position relative to the p-dioxane, and there is no steric hindrance, the shielding is almost identical (-0.28 vs.

-0.26 ppm).

The IMI in pure ethers and between different ethers indicates that the three ethers which were analysed interact as both proton donors and proton acceptors. The methoxy group interacts as a proton donor and the intensity of the interaction has not been changed by the reminder of the molecule (methoxy in IPME and in EGDME has deshielding of 0.14 and 0.12 ppm in DIPE). The intensity of the interaction between the methoxy group and the oxygen depends on the structure of the alkyl segments of the ehter which is the electron donor. The pattern of this change (methoxy carbon in IPME is deshielded 0.09 ppm by IPME, 0.12 ppm by DEE and 0.14 ppm by DIPE) does not suggest, however, that this interaction is sensitive to the steric hindrance by a single isopropyl group in IPME, or by two isopropyl groups in DIPE. To the contrary it seems to be enhanced by the higher electron donating power of the alkyl groups (10). Interaction with DnBE, however, induces only negligible deviation, suggesting a dispersive type interaction, which can be explained only by the steric hindrance from the flexible n-butyl segments.

The ethoxy group interacts through its β hydrogens, the intensity of this interaction being apparently the same as that of the methoxy group. The αCH_2 group in the ethoxy group apparently cannot form hydrogen bonds with the oxygen in ethers. Similarly the αCH group in IPME is not engaged in the hydrogen bond, with a possible exception of solution in p-dioxane. The βCH_3 group in IPME does not appear to be engaged in any specific interaction except the very weak interaction

with the most accessible oxygen in DEE. It may be expected that the cohesive interactions in PVME are governed by a similar set of relations as the interactions of low molecular weight ethers. The principal interaction would then be the hydrogen bond between the methoxy group in one and the oxygen in another repeat unit. The two other structural groups αCH and βCH_2 can apparently be involved in the dispersive interactions.

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C H A P T E R VIII

INTERMOLECULAR INTERACTIONS OF POLY(VINYL METHYL ETHER) AND POLYSTYRENE

Introduction

The change of the NMR chemical shift of polymers has been attributed to the intermolecular interaction in only a few cases (1-5). Only in two of them this change has been applied to identify the character of the IMI (3,4). None of these works has applied Rummens plot (6) to separate the contributions of the specific and nonspecific IMI. They have, however, indicated that chemical shifts of polymers are sensitive to IMI in a manner resembling that of the low molecular weight compounds.

This chapter reports about an analysis of the solvent-induced changes of chemical shifts, SIS, of polymers by applying the Rummens approach. Based on these SIS some of the intermolecular interactions have been characterized for the two polymers: poly(vinyl methyl ether), PVME, and polystyrene, PS.

In our work, we have modified Rummens approach (6,7) by limiting the selection of the dispersive solvents to linear alkanes only. This removes the ambiguity about the character of the interaction between the solvent and the solute and also reduces the number of possible biasses. The need to work with nonpolar solvents poses a limit on the application of the Rummens plot for polymers, since only a very limited number of polymers, of any

significant molecular weight, may be dissolved in them.

Interactions of Poly(vinyl methyl ether)

One of polymers that can be dissolved in n-alkanes is PVME. Its solubility, however, does depend very much on the molecular weight, MW, and on the temperature. Two samples of PVME, of different molecular weights, have been applied in this study. The sample of lower molecular weight, PVME(LMW), was obtained from Polyscience, Inc., Warrington, Pennsylvania. Gel permeation chromatography, in TMF at 25°C, indicates weight and number average molecular weights, of M_w = 14,000 and M_n = 2,000 respectively, i.e. an M_w/M_n of 7.0, calculated as for PS. Saturated solutions of this polymer in n-alkanes at 29 ± 0.5°C contain enough polymer to allow the ^{13}C NMR spectrum to be obtained at 31°C. The sample of higher molecular weight, PVME(HMW), was obtained from GAF Corp., New York. It has a reported viscosity average molecular weight, M_v, of 235,000. Gel permeation chromatography in THF at 25°C indicates a weight average molecular weight, M_w, calculated as if the polymer were PS, of 139,200 and a number average molecular weight, M_n of 14,800, i.e. an M_w/M_n of 9.4. A saturated solution of this polymer in n-alkanes at 29 ± 0.5°C contain enough polymer to allow the recording of the ^{1}H NMR spectra. The concentration is, however, too small for the ^{13}C NMR. In order to achieve concentration sufficient for the determination of ^{13}C NMR, saturated solutions of this polymer in n-alkanes were prepared at 70 ± 0.5°C and the spectra were recorded at 75 ± 0.5°C. The ^{13}C and ^{1}H NMR

spectra for PVME recorded either for different molecular weights or at very different temperatures can not be directly compared. Their comparison may, however, provide some information which would not be available from the spectra of only one kind.

For every carbon, and for those hydrogens in PVME whose peaks can be separated, chemical shifts in n-alkanes show a remarkable linear dependence on g^2, irrespective of the temperature and of the M_w of the solute (Tables VIII-1 to VIII-3).

For PVME(HMW) the ^1H Si for α CH and OCH_3 (Table VIII-1) have similar values, indicating that the accessibilities of the hydrogen and the polarizabilities of the C-H bonds are similar. The large difference between the ^{13}C Si for α CH and OCH_3 (Table VIII-1) may, however, be explained as either higher polarity of the C-H bond in OCH_3 or as its higher accessibility for alkanes. The ^1H Si values (Table VIII-2) suggest the second explanation as more probable. The ^{13}C Si for α CH and OCH_3 of PVME(LMW) at 31°C (Table VIII-3) are somewhat higher (13 and 6% respectively) then the corresponding values for PVME(HMW) at 75°C, but the ratio of their values is essentially the same. This suggests that the molecular weight has a very significant adverse effect on the solubility of the polymer but it does not affect the differences which exist between the two structural groups in the repeat unit.

It is interesting to note that the ^{13}C Si values for α CH and OCH_3, in both PVME, are practically the same as the corresponding Si values of IPME (49.63 and 81.83 ppm, respectively). This underlines

TABLE VIII-1

^{13}C NMR Chemical Shift for PVME(HMV) in Different Solvents*

No	Solvent	g^2	αCH			OCH_3			$\beta CH_3(m)$			$\beta CH_3(r)$		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C7	3.63	8.46			-11.51			-26.45			-28.28		
2	C7	3.63	8.50			-11.55								
3	C7	3.63	8.50			-11.55			-28.29					
4	C7	3.63	8.49			-11.56								
5	C8	3.78	8.58			-11.45			-26.40			-28.22		
6	C8	3.78	8.54											
7	C8	3.78	8.58			-11.46								
8	C8	3.78	8.52											
9	C9	3.87	8.56			-11.40						-28.18		
10	C9	3.87	8.59									-28.19		
11	C9	3.87	8.62			-11.39								
12	C9	3.87	8.63											
13	C10	3.96	8.61			-11.29						-28.18		
14	C10	3.96	8.62			-11.31								
15	C10	3.96	8.65			-11.33								
16	C10	3.96	8.65											
17	C10	3.96	8.66											
18	C10	3.96	8.66						-26.31					
19	C11	4.04	8.66			-11.25								
20	C11	4.04	8.67			-11.22								
21	C11	4.04	8.69			-11.23			-26.32			-28.12		
22	C12	4.11	8.66			-11.18			-26.23			-28.09		
23	C12	4.11	8.70			-11.19			-26.24			-28.11		
24	C12	4.11	8.71			-11.18								
25	C12	4.11	8.73			-11.20								
26	C13	4.15				-11.15								
27	C13	4.15							26.23			-28.08		
26	C13	4.15										-28.09		
29	C15	4.24	8.79	**			**		-26.19	**		-28.09		
												-28.02	**	
30	CCl_4	4.62	9.00	8.96	0.04	-10.62	-10.80	0.18	-25.92	-26.03	0.11	-27.64	-27.90	0.26
			(8.91)		(-0.05)							-27.95		(-0.05)
31	CCl_4	4.62	9.02	8.96	0.06	-10.63	-10.80	0.17	-25.93	-26.03	0.10	-27.67		0.23
			(8.93)		(-0.03)							-27.97	-27.90	(-0.07)
32	C_6H_6	5.17	8.50	9.20	-0.70	-11.40	-10.39	-1.01	-26.44	-25.79	-0.65	-28.16		-0.47
												-28.36	-27.69	(-0.67)

*All values at 75°C, relative to the external standard (10 vol% p-dioxane in DMSO-d_6 corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) αCH: correlation 0.961 for the equation $\delta = 6.80 + 46.39\ g^2$ (ppm); b) OCH_3: correlation 0.993 for the equation $\delta = -14.31 + 75.83\ g^2$ (ppm); c) $\beta CH_2(m)$: correlation 0.981 for the equation $\delta = -28.05 + 43.80\ g^2$ (ppm); d) $\beta CH_2(r)$: correlation 0.987 for the equation $\delta = -29.71 + 39.13\ g^2$ (ppm).

TABLE VIII-2

^{1}H NMR Chemical Shifts for PVME(HMW) in Different Solvents*

No	Solvent	g^2	αCH			βCH_3		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C6	3.47	3.04			-0.85		
2	C6	3.47	3.00			-0.85		
3	C6	3.47	3.02			-0.85		
4	C7	3.63	3.06			-0.76		
5	C7	3.63	3.04			-0.76		
6	C7	3.63	3.05			-0.76		
7	C7	3.63	3.06			-0.76		
8	C8	3.78	3.15			-0.70		
9	C9	3.87	3.15			-0.68		
10	C9	3.87	3.18					
11	C10	3.96	3.19			-0.66		
12	C10	3.96	3.21					
13	C11	4.04	3.25			-0.60		
14	C11	4.04	3.25			-0.60		
15	C12	4.10	3.29			-0.56		
16	C13	4.15	3.32			-0.58		
17	C13	4.15	3.31			-0.58		
18	C16	4.26				-0.51		
19	C16	4.26		**		-0.50	**	
20	C_6H_{12}	4.15	3.27	3.30	-0.03	-0.61	-0.56	-0.05
21	CCl_4	4.62	4.00	3.51	0.49	0.04	-0.37	0.41
22	$CDCl_3$	4.43	4.10	3.42	0.48	0.36	-0.44	0.80
23	2CP	3.51	3.38	3.02	0.36	-0.54	-0.82	0.28
24	TBC	3.60	3.19	3.06	0.13	-0.61	-0.78	0.17
25	C_6D_6	5.17	3.19	3.75	-0.56	-0.62	-0.14	-0.48
26	TOL	5.12		3.73		-0.90	-0.16	-0.74
27	CUM	5.05		3.69		-0.77	-0.19	-0.58
28	CUM	5.05		3.69		-0.77	-0.19	-0.58
29	C_2HCl_3	4.84	3.33	3.60	0.27	-0.58	-0.28	-0.30
30	C_2Cl_4	5.24	3.37	3.78	0.41	-0.42	-0.11	-0.31

*All values at 37°C, relative to the external standard (10 vol % H_2O in DMSO-d_6), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) αCH: correlation 0.9845 for the equation $\delta = 1.47 + 44.02\ g^2$ (ppm); b) OCH_3: correlation 0.9927 for the equation $\delta = -2.26 + 41.07\ g^2$ (ppm).

TABLE VIII-3

^1H NMR Chemical Shift for PVME(LMW) in Different Solvents*

No	Solvent	g^2	αCH			$-OCH_3$			$\beta CH_2(m)$			$\beta CH_2(r)$		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C6	3.47	7.85			-11.97			-27.04			-29.06		
2	C7	3.63	7.89			-11.88			-27.01			-29.03		
3	C8	3.78	7.97			-11.74			-26.97			-28.97		
4	C8	3.78	7.98			-11.76			-26.97			-28.98		
5	C9	3.87	8.04			-11.67			-26.93			-28.94		
6	C10	3.96	8.09			-11.61			-26.91			-28.92		
7	C13	4.15	8.12			-11.45			-26.80			-28.88		
8	C13	4.15	8.19			-11.42			-26.79			-28.89		
9	C16	4.26	8.25			-11.36			-26.83			-28.80		
10	C16	4.26	8.23			-11.36			-26.81			-28.84		
11	C_6H_{12}	4.15	8.06	8.18	-0.12	-11.66	-11.45	-0.21	-26.89	-26.83	-0.06	-28.83	-28.87	0.04
12	IPME	3.24	7.72	7.70	0.02	-11.90	-12.18	0.28	-27.24	-27.13	-0.11	-29.21	-29.14	-0.07
13	IPME	3.24	7.72	7.70	0.02	-11.97	-12.18	0.21	-27.29	-27.13	-0.16	-29.21	-29.14	-0.07
14	DEE	3.16	7.61	7.66	-0.05	-11.99	-12.24	0.25	-27.27	-27.16	-0.11	-29.20	-29.16	-0.06
15	DIPE	3.38	7.67	7.78	0.11	-11.98	-12.06	0.08	-27.25	-27.09	-0.16	-29.44	-29.09	-0.35
15	CCl_4	4.62	8.43	8.43	0.00	-10.69	-11.07	0.38	-26.32	-26.68	0.36	-28.37	-28.73	0.36
17	$CHCl_3$	4.43	8.76	8.33	0.43	-10.16	-11.22	1.06	-26.17	-26.74	0.57	-28.24	-28.78	0.54
18	C_2HCl_3	4.84	8.13	8.54	0.41	-11.34	-10.89	-0.45	-26.76	-26.60	-0.16	-28.76	-28.66	-0.10
19	C_2Cl_4	5.24	8.20	8.75	0.55	-10.99	-10.57	-0.41	-26.56	-26.47	-0.09	-28.65	-28.54	-0.11
20	C_6H_6	5.17	7.88	8.71	-0.84	-11.69	-10.63	-1.06	-27.06	-26.50	-0.56	-20.08	-28.57	-0.51
21	TOL	5.12	7.94	8.69	-0.75	-11.68	-10.67	-1.01	-26.90	-26.51	-0.39	-29.04	-28.58	-0.46
22	CUM	5.05	8.12	8.65	-0.53	-11.31	-10.72	-0.59	-26.79	-26.54	-0.25	-28.80	-28.60	-0.20

*All values at 31°C, relative to the external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) αCH: correlation 0.9950 for the equation $\delta = 6.00 + 52.49\ g^2$ (ppm); b) OCH_3: correlation 0.9978 for the equation $\delta = -14.78 + 80.27\ g^2$ (ppm); c) $\beta CH_2(m)$: correlation 0.9656 for the equation $\delta = -28.20 + 32.89\ g^2$ (ppm); d) $\beta CH_2(r)$: correlation 0.9810 for the equation $\delta = -30.09 + 29.53\ g^2$ (ppm).

the chemical character, and the polarity of the group as the most important parameter determining the intensity of the dispersive interaction.

For both of PVME only a small difference exists between ^{13}C Si for α- and the two β-carbons (Tables VIII-1 and VIII-3). This suggests that the C-H in βCH_2 are polarized comparably to the αCH. Since the extent to which a bond may be polarized does not depend much on stereoregularity (8), the small difference (~ 10%) in Si between racemic, $\beta CH_2(r)$ and meso, $\beta CH_2(m)$ probably reflects somewhat reduced access to $\beta CH_2(m)$. There appears to be no report indicating that chain configuration in PVME affects accessibility to β-hydrogen. It has been reported, however, that the erythro-meso β-hydrogen in PVME may be in the vicinity of the methoxy group (9) and that the δ interaction may influence NMR spectra of polymers (10). ^{13}C Si values for PVME(LMW) at 31°C are both reduced relative to ^{13}C Si for PVME(HMW) at 75°C. It is interesting, however, that the relative reductions are practically identical (24.9% for $\beta CH_2(r)$ and 24.5% for $\beta CH_2(m)$), so the mutual ratio of the two slopes remain the same (1.12 for PVME(HMW) and 1.11 for PVME(LMW)). An explanation for the identical ratios in the two different molecular weights and at the two temperatures, may be that whatever the effect of the two variables, they affect both stereo configurations in the same way. However, the reason for the considerable reduction of the Si for βCH_2, as opposed to the small increases for αCH and OCH_3, is not obvious at this moment. The fact that the reduction occurs for the polymer of lower

MW suggests that the chief reason for it is the lower temperature. Since the reduction occurs on the βCH_2 it possibly has to do with the existence of some kind of the repeat unit-to-repeat unit steric hindrances. It may be the already mentioned δ interaction (10), which becomes more pronounced, as the conformational mobility of the polymer decreases, at lower temperatures.

When PVME is dissolved in benzene all its nuclei show upfield deviations from the VDWL (Tables VIII-1 to VIII-3 and Figures VIII-1 to VIII-4 and VIII-6 to VIII-9). This is the same effect as seen for the methoxy group in isopropyl methyl ether, IPME (Chapter VII, Table VII-2). This suggests that the average C-H group from PVME approaches a benzene molecule in the direction orthogonal to the ring (11). The nature of this interaction is still controversial (12,13). To better understand the mechanism of this interaction NMR spectra have also been recorded for PVME(HMW) dissolved in mixtures of benzene and n-dodecane at five different concentrations (Figure VIII-5). For all carbons, except methoxy, the chemical shifts change linearly with the volume fraction of benzene in the solvent. This indicates dispersive interactions between the corresponding groups in PVME and benzene (12,14). Chemical shifts for OCH_3 level-off at high benzene concentrations indicating the preferable solvation and, probably, an IMI stronger than dispersive. Deviation suggests a π-hydrogen bond between the methoxy hydrogen and benzene (15-18). This is in agreement with findings for the solutions of IPME in the mixtures of benzene and n-hexadecane (Chapter VI, Table VI-12 and Figure VI-3) and with the

Fig. VIII-1. Rummens plot of ^{13}C NMR chemical shifts for α-methyne carbon of PVME(HMW) in different solvents.

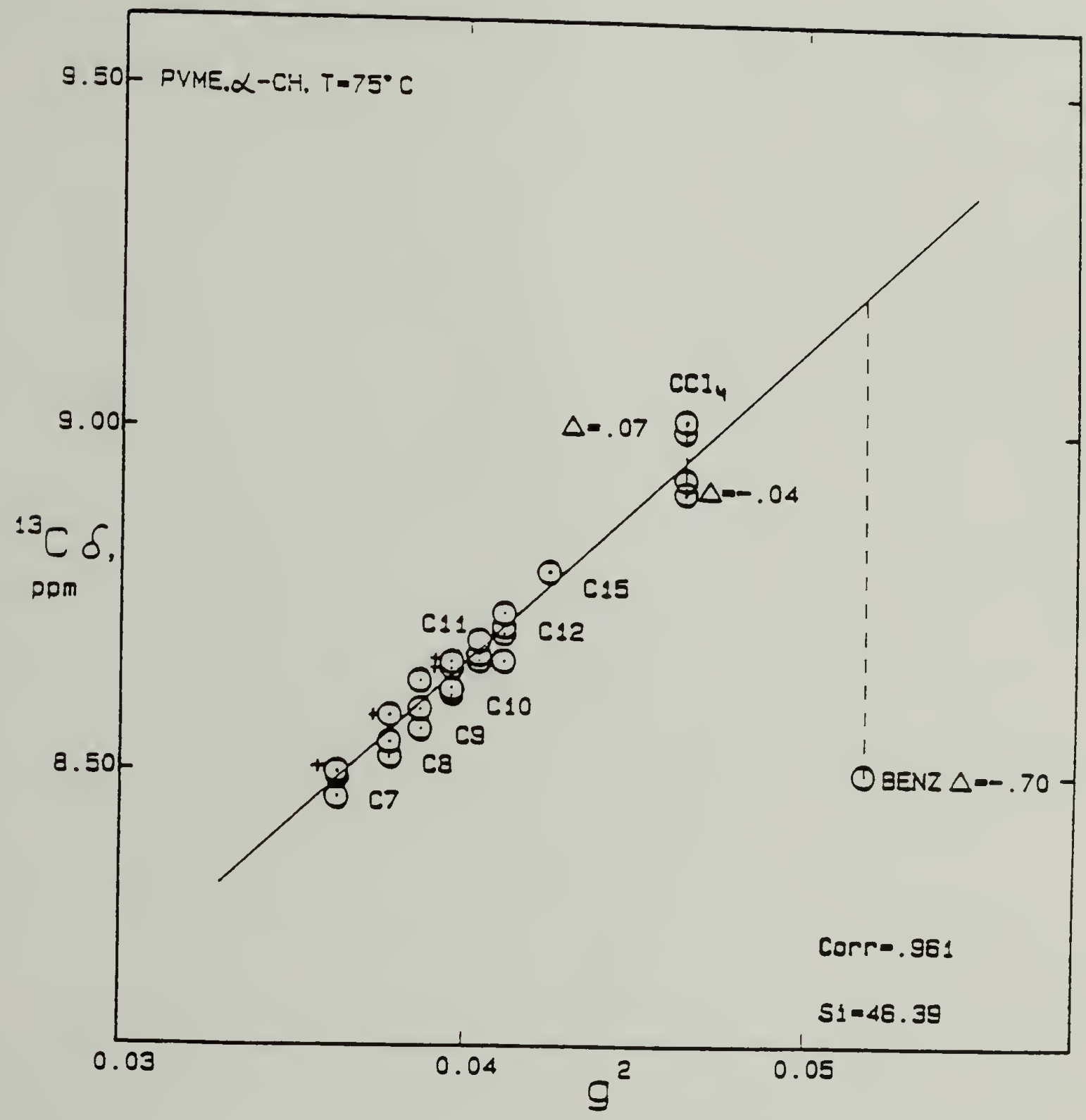

PVME.α-CH. T=75° C
9.50
9.00
8.50
^{13}C δ, ppm
CCl_4
Δ=.07
Δ=-.04
C15
C11
C12
C10
C9
C8
C7
BENZ Δ=-.70
Corr=.961
Si=46.39
0.03
0.04
0.05
g^2

Fig. VIII-2. Rummens plot of ^{13}C NMR chemical shifts for methoxy carbon of PVME(HMW) in different solvents.

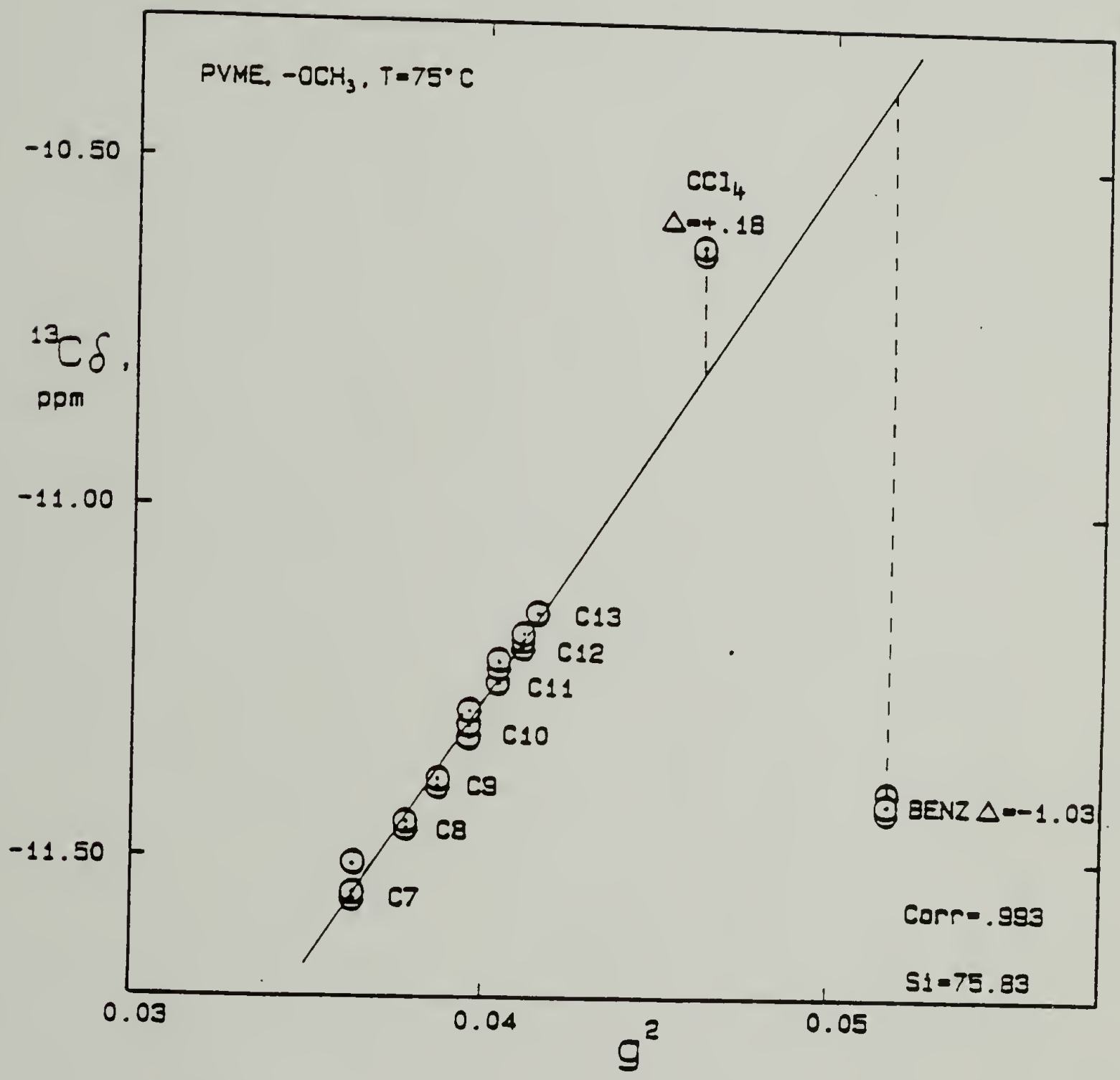

PVME, -OCH3, T=75°C
-10.50
-11.00
-11.50
13C δ, ppm
CCl4
Δ=+.18
C13
C12
C11
C10
C9
C8
C7
BENZ Δ=-1.03
Corr=.993
Si=75.83
0.03
0.04
0.05
g2

Fig. VIII-3. Rummens plot of ^{13}C NMR chemical shifts for racemic β-methylene carbon of PVME(HMW) in different solvents.

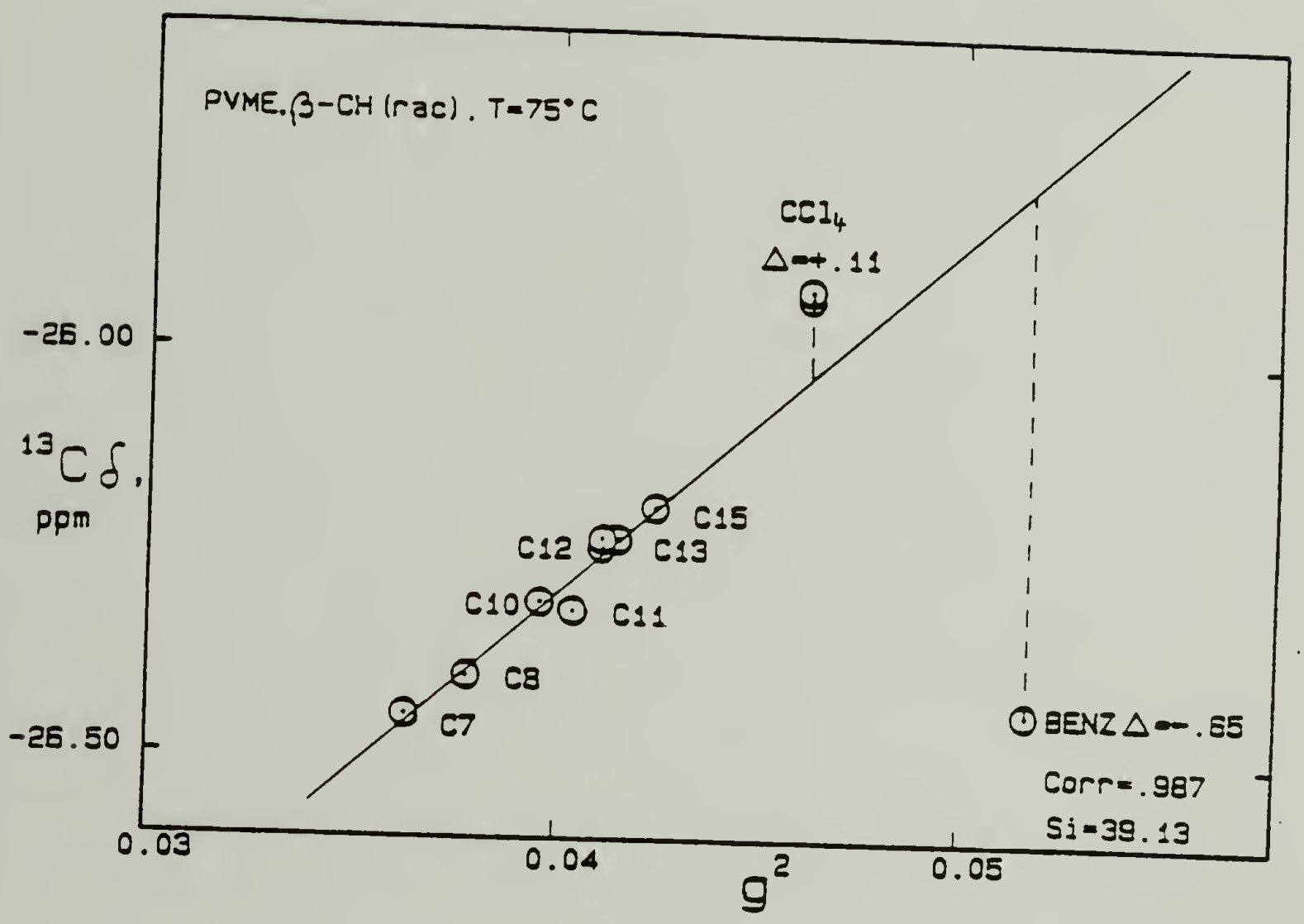

PVME.β-CH (rac) . T=75° C
CCl4
Δ=+.11
-26.00
13C δ, ppm
C15
C12
C13
C10
C11
C8
C7
-26.50
BENZ Δ=-.65
Corr=.987
Si=39.13
0.03
0.04
0.05
g2

Fig. VIII-4. Rummens plot of ^{13}C NMR chemical shifts for meso β-methylene carbon of PVME(HMW) in different solvents.

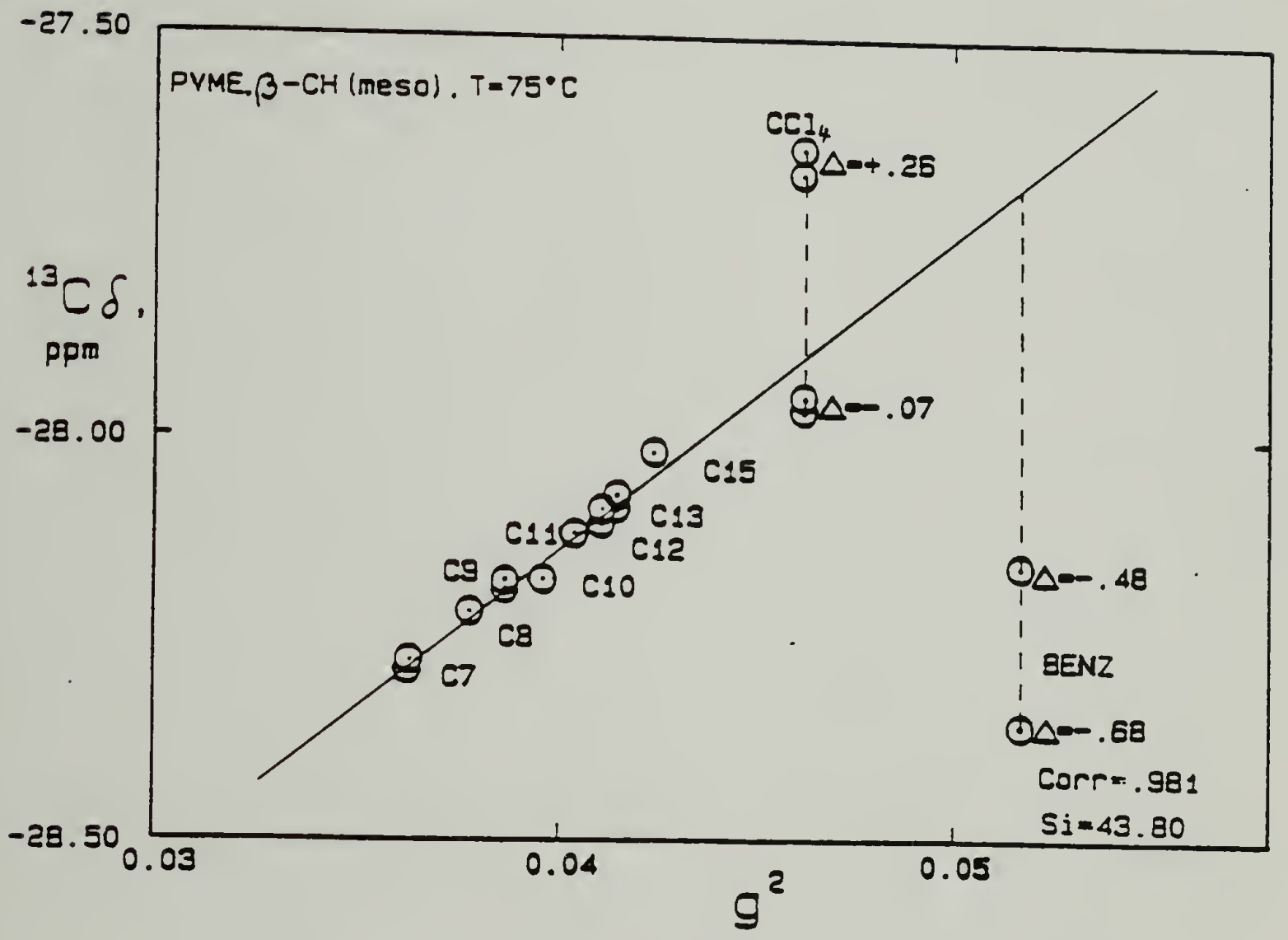

PVME β-CH (meso), T=75°C
$^{13}C\delta$, ppm
-27.50
-28.00
-28.50
0.03
0.04
0.05
g^2
CCl_4
Δ=+.25
Δ=-.07
Δ=-.48
BENZ
Δ=-.68
Corr=.981
Si=43.80
C15
C13
C12
C11
C10
C9
C8
C7

Fig. VIII-5. The ^{13}C NMR chemical shifts for carbons of PVME(HMW) in mixtures of n-dodecane and benzene.

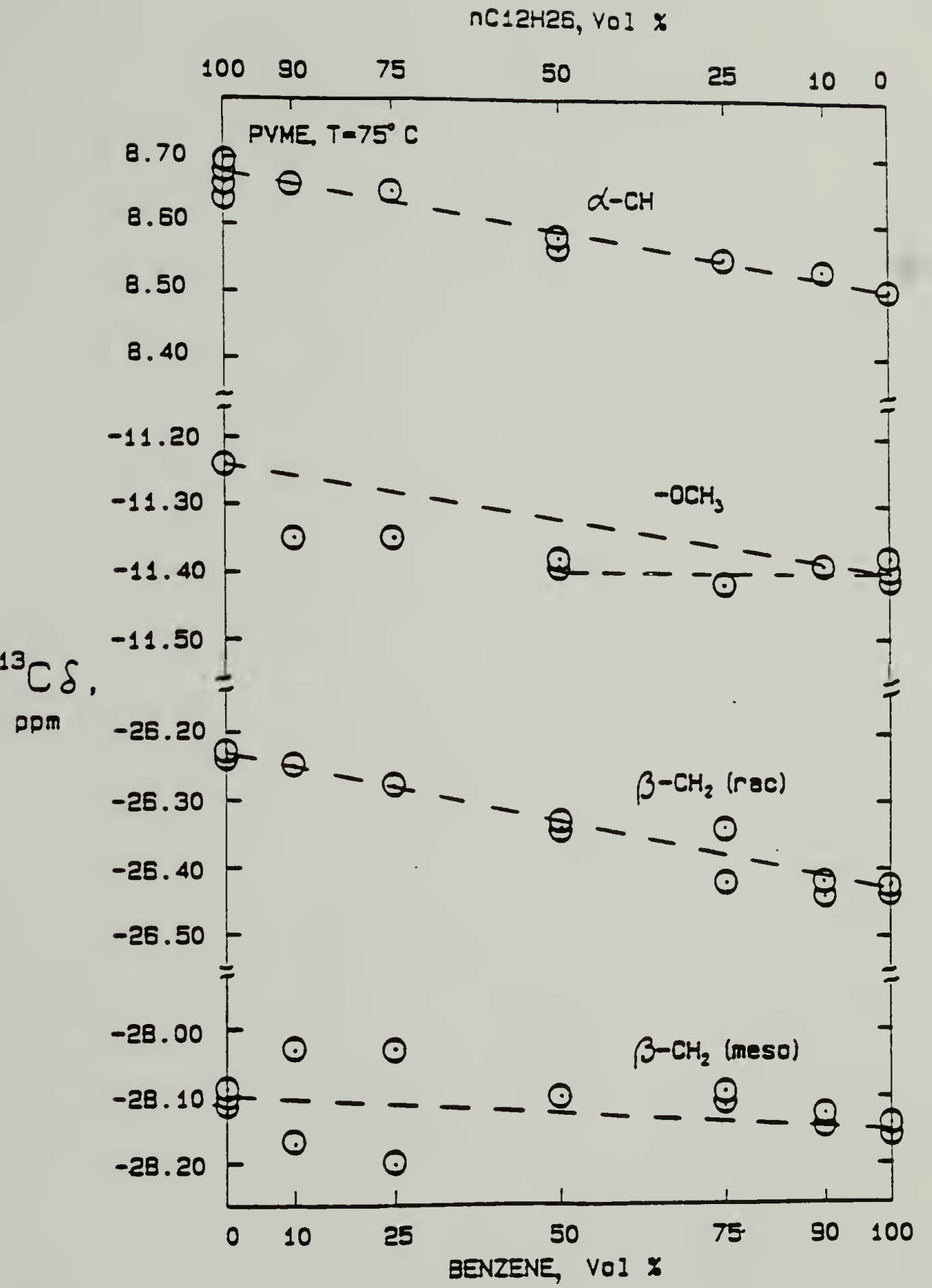

nC12H26, Vol %
100 90 75 50 25 10 0
PVME, T=75° C
8.70
8.60
8.50
8.40
α-CH
-11.20
-11.30
-11.40
-11.50
-OCH3
13C δ, ppm
-26.20
-26.30
-26.40
-26.50
β-CH2 (rac)
-28.00
-28.10
-28.20
β-CH2 (meso)
0 10 25 50 75 90 100
BENZENE, Vol %

Fig. VIII-6. Rummens plot of ^{13}C NMR chemical shifts for α-methylene carbon of PVME(LMW) in different solvents.

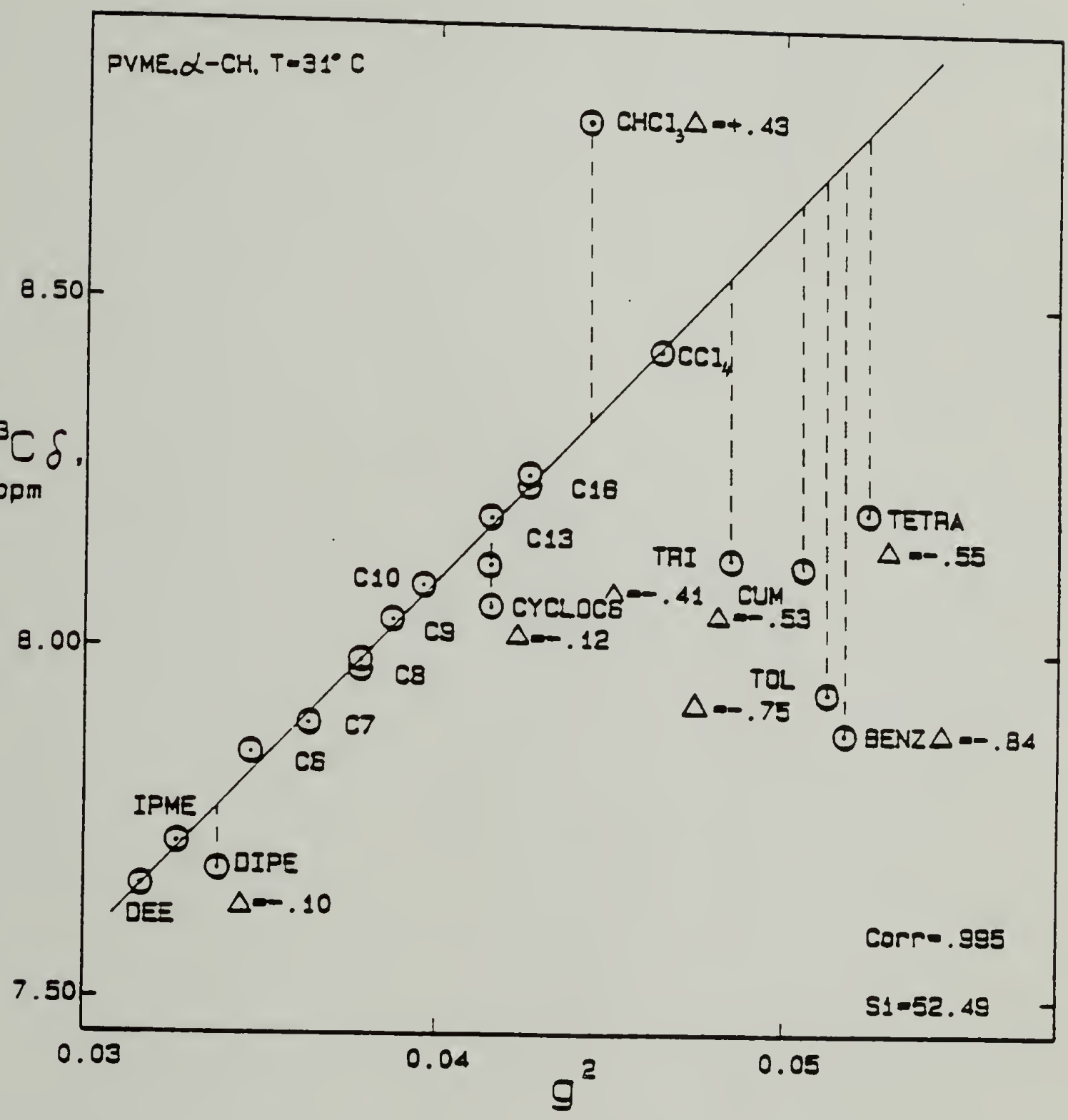

PVME.α-CH. T=31° C
CHCl3 Δ=+.43
CCl4
C18
C13
C10
C9
C8
C7
C6
CYCLOC6
Δ=-.12
TRI
Δ=-.41
CUM
Δ=-.53
TETRA
Δ=-.55
TOL
Δ=-.75
BENZ Δ=-.84
IPME
DIPE
Δ=-.10
DEE
Corr=.995
Si=52.49
8.50
8.00
7.50
13C δ, ppm
0.03
0.04
0.05
g2

Fig. VIII-7. Rummens plot of ^{13}C NMR chemical shifts for methoxy carbon of PVME(LMW) in different solvents.

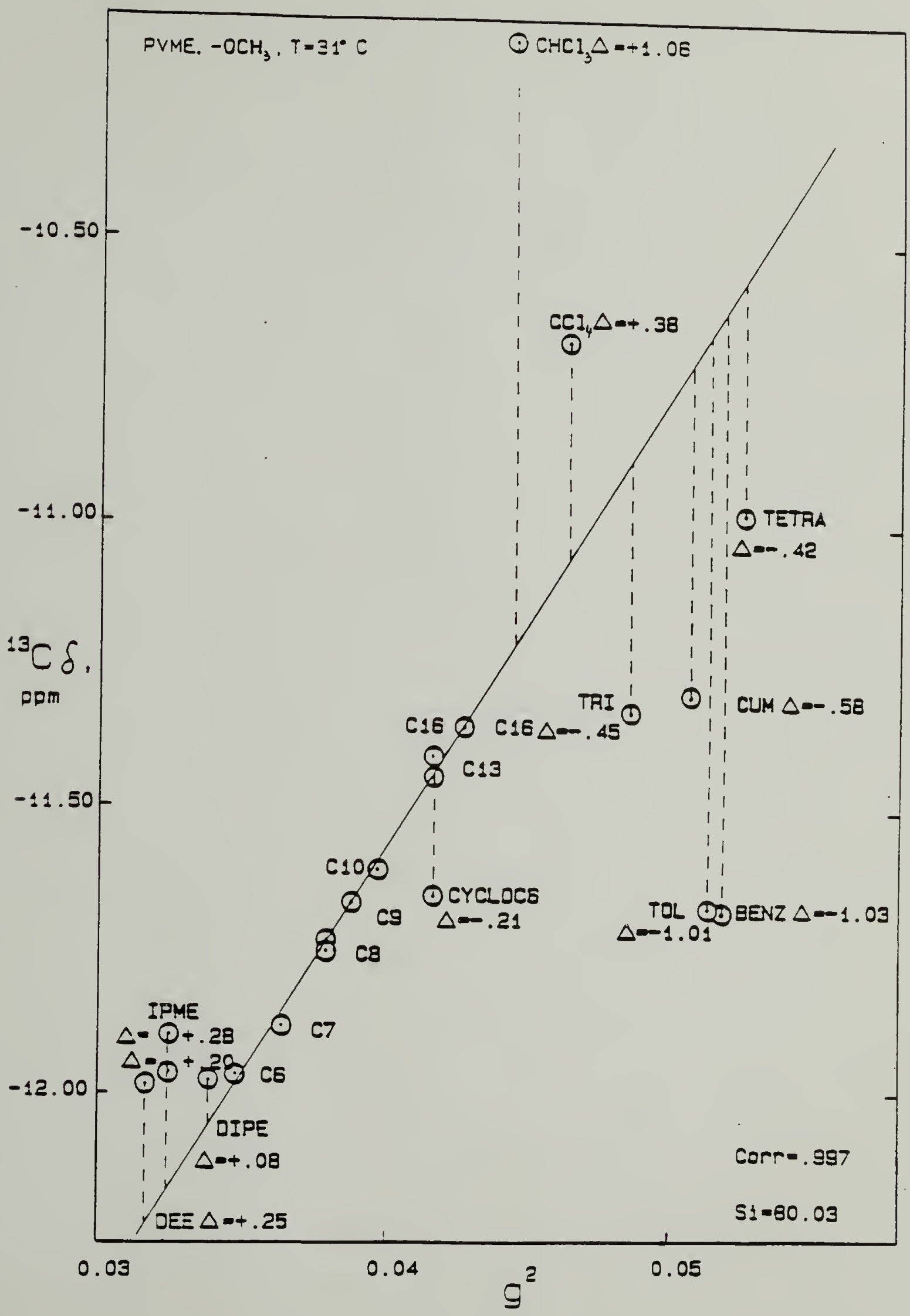

PVME. -OCH3 . T=31° C
CHCl3 Δ=+1.06
CCl4 Δ=+.38
TETRA
Δ=-.42
TRI
CUM Δ=-.58
C16
C16 Δ=-.45
C13
C10
CYCLOC6
Δ=-.21
C9
C8
TOL
BENZ Δ=-1.03
Δ=-1.01
IPME
Δ=+.28
Δ=+.20
C7
C6
DIPE
Δ=+.08
DEE Δ=+.25
Corr=.997
Si=80.03
-10.50
-11.00
-11.50
-12.00
13C δ, ppm
0.03
0.04
0.05
g2

Fig. VIII-8. Rummens plot of ^{13}C NMR chemical shifts for racemic β-methylene carbon of PVME(LMW) in different solvents.

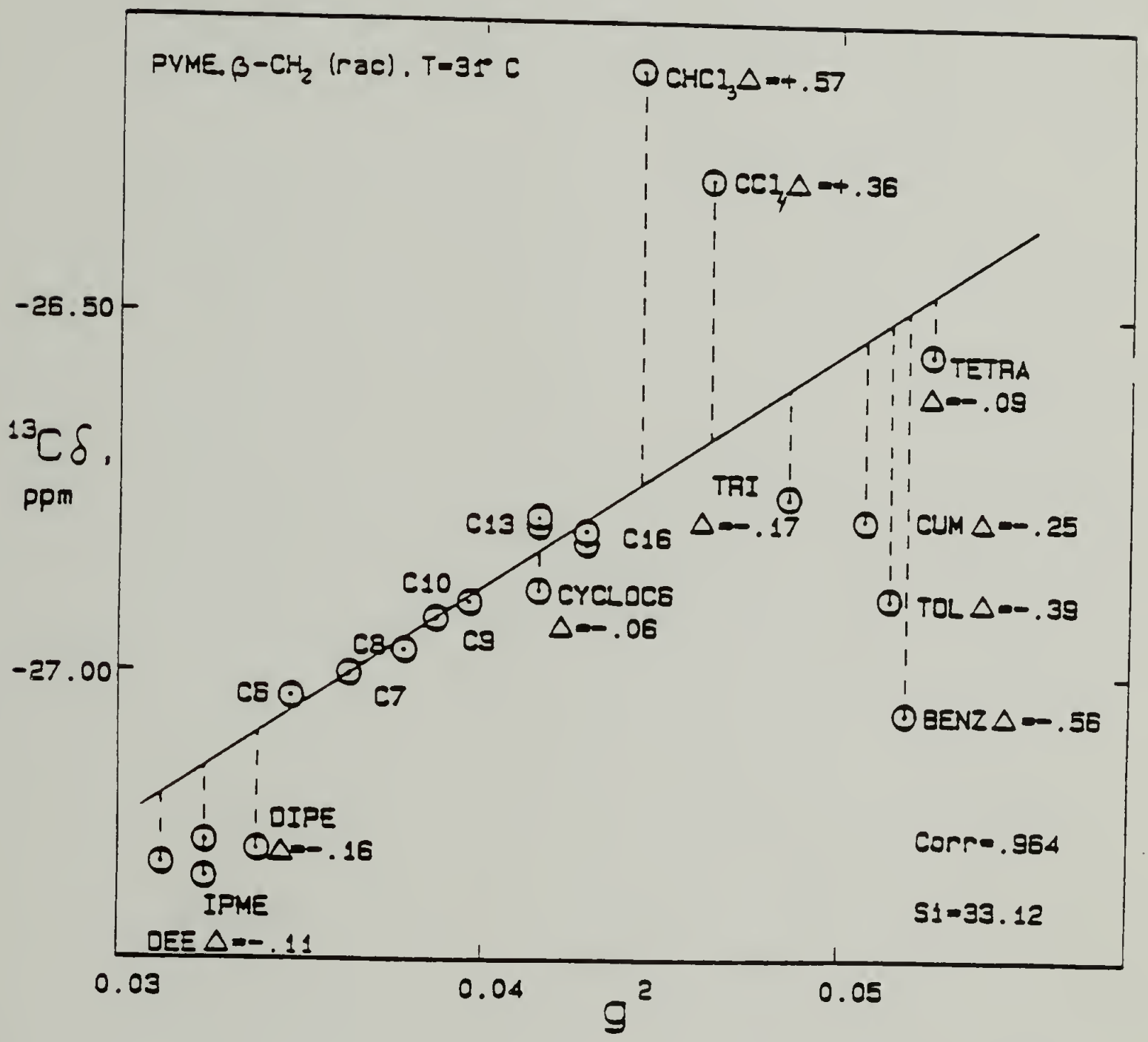
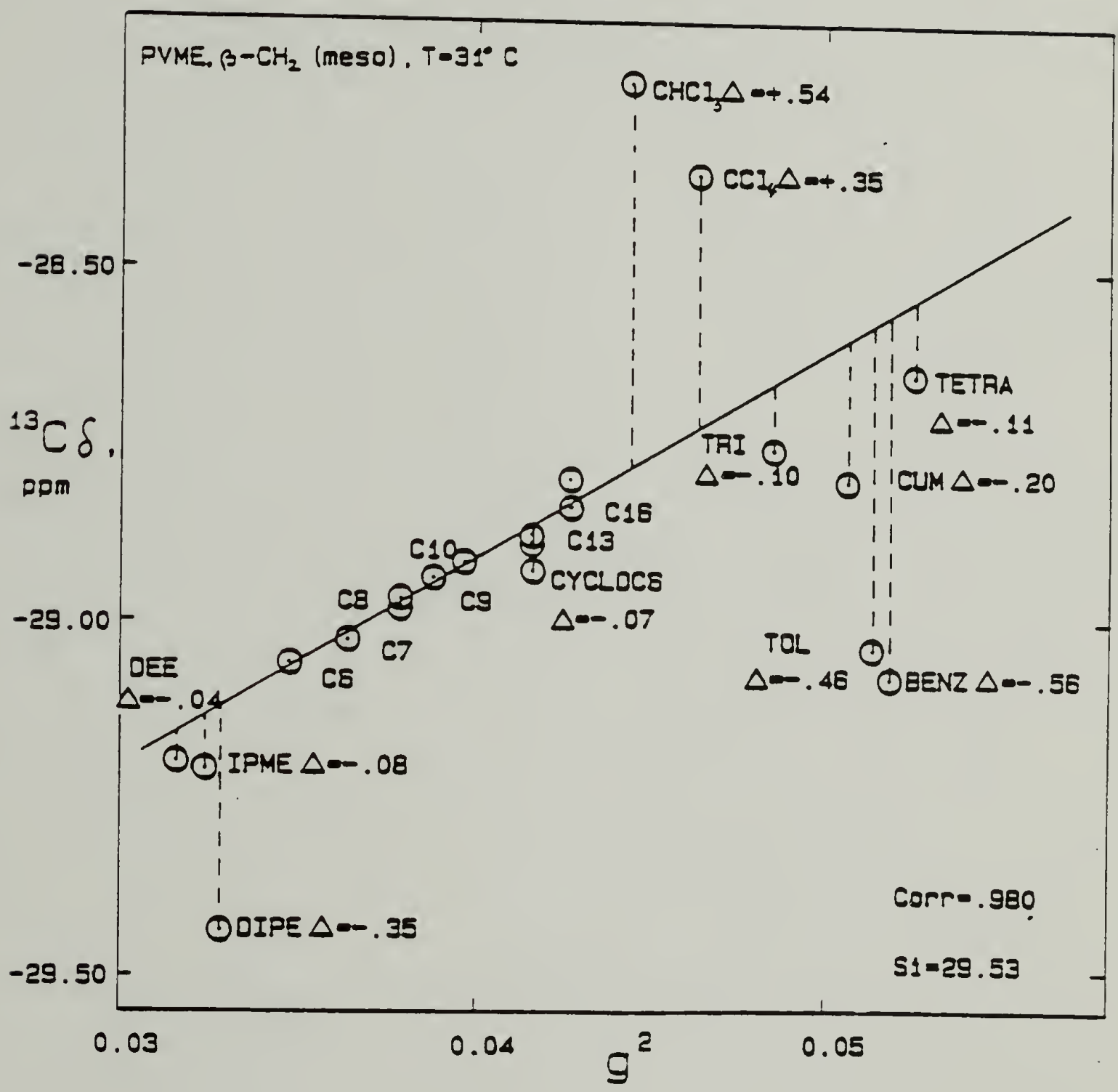

PVME β-CH2 (rac). T=31° C
CHCl3 Δ=+.57
CCl4 Δ=+.36
-26.50
-27.00
13C δ, ppm
TETRA Δ=-.09
TRI Δ=-.17
CUM Δ=-.25
TOL Δ=-.39
BENZ Δ=-.56
CYCLOC6 Δ=-.06
C13
C16
C10
C9
C8
C7
C6
DIPE Δ=-.16
IPME
DEE Δ=-.11
Corr=.964
Si=33.12
0.03
0.04
0.05
g2

Fig. VIII-9: Rummens plot of ^{13}C NMR chemical shifts for meso β-methylene carbon of PVME (LMW) in different solvents.


PVME. β-CH2 (meso). T=31° C
CHCl3 Δ=+.54
CCl4 Δ=+.35
-28.50
13C δ, ppm
TETRA
Δ=-.11
TRI
Δ=-.10
CUM Δ=-.20
C16
C13
C10
CYCLOC6
Δ=-.07
C8
C9
C7
C6
-29.00
DEE
Δ=-.04
TOL
Δ=-.46
BENZ Δ=-.56
IPME Δ=-.08
DIPE Δ=-.35
Corr=.980
S1=29.53
-29.50
0.03
0.04
0.05
g2

findings for solution of benzene in IPME (Chapter VI, Table VI-1). The intensities of the benzene-induced deviations from VDWL for carbons in the two PVME are very similar (Tables VIII-1 and VIII-3). This similarity suggests that the IMI between the corresponding groups and benzene must be very weak. The benzene-induced deviations from VDWL for αCH and OCH_3 carbons in IPME have practically the same intensities (-0.77 and -1.03 ppm, respectively) as the corresponding deviations for the two PVME. As in the case of similar Si values it is apparent that the structural group properties have the decisive effect on the character and the intensity of the IMI.

If the interaction between PVME and benzene were to occur through a dipole (solute)-quadrupole (benzene) interaction (13), then the strongest interaction would be between the electro-positive "edges" of the benzene ring and the electronegative oxygen in the ether link. This would prevent, electrostatically, any other benzene molecule from approaching the C-H in the methoxy group. As a result both OCH_3 and αCH would show a downfield anisotropic deviation (11) which would be opposite to the experimental results reported in Tables VIII-1 and VIII-3.

Data available are not sufficient to determine completely and positively the character of the interactions between CCl_4 and PVME. Certain considerations can, however, be made.

The different character of SIS for OCH_3 and αCH carbons (Tables VIII-1 and VIII-3) suggests that the interaction of CCl_4 with oxygen

(19-21) is not of major importance.

CCl_4 as solvent for PVME(HMW) induces a small deshielding of $-OCH_3$ carbons at 75°C and a moderate deshielding of the corresponding hydrogen at 37°C. It also induces a moderate deshielding of the OCH_3 carbon in PVME(LMW) at 31°C. Those deshieldings suggest the interaction with the hydrogen from OCH_3. This may be either a polar IMI or a weak hydrogen bond (19). This is in agreement with the findings for ethers of low molecular weight dissolved in CCl_4 (Chapter VII, Tables VII-1 to VII-3) and for CCl_4 dissolved in ethers (Chapter IV, Table IV-1). It is interesting to note that the moderate deshielding of OCH_3 carbon in IPME dissolved in CCl_4 has the intensity (0.27 ppm) corresponding to the effect of CCl_4 on PVME.

When PVME(LMW) is dissolved in CCl_4 at 31°C its αCH shows in ^{13}C NMR a singlet at VDWL. PVME(HMW) at 75°C, however, exhibits in ^{13}C NMR a reproducible doublet, with peaks of similar intensities. It is nearly symmetrical about the VDWL, with deviations of negligible intensities. (Table VIII-1 and Figure VIII-1). In ^{1}H NMR PVME(HMW) has a singlet indicating a moderate deshielding (0.49 ppm). This deshielding suggests a specific IMI, possibly a hydrogen bond or a polar interaction. This is in agreement with the reported findings that the dyad configuration of PVME does not have any interference with steric accessibility of αCH (22,23). The reason for the different patterns of the SIS in ^{13}C NMR is not clear at this time. This pattern of SIS is also different from the effect of CCl_4 on IPME where it induces a weak (0.24 ppm) deshielding of α carbon. All β carbons

in both PVME show weak to moderate deshielding by CCl_4 as does β carbon in IPME. They suggest the interaction of CCl_4 with β C-H bond. An exception occurs for βCH_2(m) in PVME(HMW) which shows two peaks, one indicating moderate deshielding and the other very weak shielding. One explanation for the peak close to VDWL may be the existence of steric hindrance which prevents CCl_4 from approaching sufficiently near. This explanation may be consistent with the already mentioned closeness of OCH_3 and βCH_2 groups in erythro-meso triads (9).

Interactions of Polystyrene

In order to understand the IMI of PS an analysis was performed on two samples, an oligomer and a PS with molecular weight 17,500. For a comparable molecular weight the solubility of PS in n-alkanes is even smaller than that of PVME. The full Rummens plot, containing the points for solutions in both n-alkanes and other solvents could be obtained for the oligomer only. The sample of the styrene oligomer, PS 600, has been obtained from Pressure Chemicals, Pittsburgh, Pennsylvania. It has M_W = 600 and narrow MW distribution. This oligomer with 5 or 6 repeat units is considered a good representative of the PS structure since it has all the structural groups characteristic for the polymer.

Besides n-alkanes the effect on the chemical shift has been analysed also for CCl_4, DEE, IPME and DIPE (Table VIII-4 and Figures VIII-10 to VIII-14).

TABLE VIII-4

^{13}C NMR Chemical Shifts for PS 600 in Different Solvents*

No	Solvent	g^2	Ci			Co,m			Cp			αC			βC		
			δcorr	δVOWL	Δ	δcorr	δVOWL	Δ	δcorr	δVDWL	Δ	δcorr	δVOWL	Δ	δcorr	δVOWL	Δ
1	C6	3.47	77.90			50.39			58.02			-24.12			-26.29		
2	C6	3.47	77.76			60.34			58.06			-24.13			-26.64		
3	C7	3.63	77.64			60.38			58.13			-24.01			-26.61		
4	C7	3.63	77.86			60.47			58.17			-24.01			-26.62		
5	C8	3.78	77.91			60.49			58.22			-23.93			-26.58		
6	C9	3.87	77.93			60.53			58.26			-23.89			-26.58		
7	C9	3.87	77.91			60.59			58.24			-23.91			-26.51		
8	C10	3.96	77.92*			60.59			58.32			-23.85			-26.45		
9	C10	3.96	77.95			60.59			58.33			-23.87			-26.45		
10	C12	4.11	78.00			60.69			58.39			-23.75			-26.35		
11	C12	4.11	77.94			60.64			58.39			-23.75			-26.39		
12	C13	4.15	78.00			60.64						-26.76			-25.41		
13	C13	4.15	78.02			60.76			58.41			-23.78			-26.41		
14	C14	4.19	78.00			60.72			58.43			-23.75			-26.38		
15	C16	4.26	78.05			60.75	**		58.48	**		-23.68	**		-26.36	**	
16	C_6H_{12}	4.15	78.01	78.01	0.00	60.56	60.60	-0.04	58.27	58.42	-0.15	-23.80	-23.75	-0.05	-26.40	-26.40	0.00
17	C_6H_6	5.12										-24.20	-23.21	-0.99	-26.77	-25.96	-0.31
18	C_6H_6	5.17										-23.98	-23.21	-0.77	-26.75	-25.96	-0.79
19	TOL	5.12										-24.01	-23.28	-0.73	-26.75	-26.02	-0.73
20	TOL	5.12										-23.97	-23.28	-0.69	-26.71	-26.02	-0.69
21	m-XYL	5.13	77.88	78.29	0.41							-24.01	-23.23	-0.77	-26.69	-25.98	-0.71
22	OPM	6.18	78.30	78.59	0.29	61.52	61.78	-0.26				-24.06	-22.68	-1.38	-26.16		
23	OEE	3.15	77.61	77.72	0.11	60.31	60.16	0.15	57.97	57.88	-0.09						
24	OEE	3.15	77.62	77.72	-0.10	60.30	60.16	0.16	58.03	57.88	0.15	-24.34	-24.27	-0.07	-26.78	-26.82	0.04
25	IPME	3.24	77.75	77.75	0.00	60.34	60.21	0.13	58.08	57.92	0.16	-24.31	-24.23	-0.08	-26.78	-26.78	0.00
26	OIPE	3.38	77.57	77.79	-0.22	60.39	60.28	0.11	58.10	58.00	0.10	-24.31	-24.15	-0.16	-26.86	-26.72	-0.14
27	CCl_4	4.62	78.37	78.14	0.23	61.31	60.95	0.36	59.12	58.67	0.45	-23.52	-23.50	-0.20	-26.10	-26.20	0.10
28	CCl_4	4.62	78.37	78.14	0.23	61.32	60.95	0.37	59.09	58.67	0.42	-23.51	-23.50	-0.01	-26.10	-26.20	0.10
29	CCl_4	4.43	78.94	78.09	0.85	61.64	60.84	0.80	59.21	58.56	0.65	-23.31	-23.60	0.29	-25.99	-26.28	0.29
30	C_2HCl_3	4.84	78.05	78.20	-0.15	60.92	61.06	-0.14	58.57	58.78	-0.21	-23.93	-23.39	-0.54	-26.53	-26.10	-0.43
31	C_2HCl_3	4.84	78.05	78.20	-0.15	60.91	61.06	-0.15	58.55	58.78	-0.23	-23.89	-23.38	-0.51	-26.50	-26.10	-0.40
32	C_2HCl_3	5.24	78.13	78.32	-0.19	60.97	61.28	-0.31	58.71	59.00	-0.29	-23.80	-23.18	-0.62	-26.36	-25.94	-0.42
33	C_2HCl_3	5.24	78.11	78.32	-0.21	60.95	61.28	-0.33	58.74	59.00	-0.26	-23.83	-23.18	-0.65	-26.35	-25.94	0.41

*All values at 31°C, relative to the external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) Ci: correlation 0.983 for the equation $\delta = 76.82 + 28.96\ g^2$ (ppm); b) Co,m: correlation 0.998 for the equation $\delta = 58.47 + 53.59\ g^2$ (ppm); c) Cp: correlation 0.994 for the equation $\delta = 56.19 + 53.71\ g^2$ (ppm); d) αC: correlation 0.986 for the equation $\delta = -25.93 + 52.81\ g^2$ (ppm); e) βC: correlation 0.989 for the equation $\delta = -28.14 + 42.16\ g^2$ (ppm)

Fig. VIII-10. Rummens plot of ^{13}C NMR chemical shifts for para carbon in PS: (○) PS 600; (△) PS 17,500.

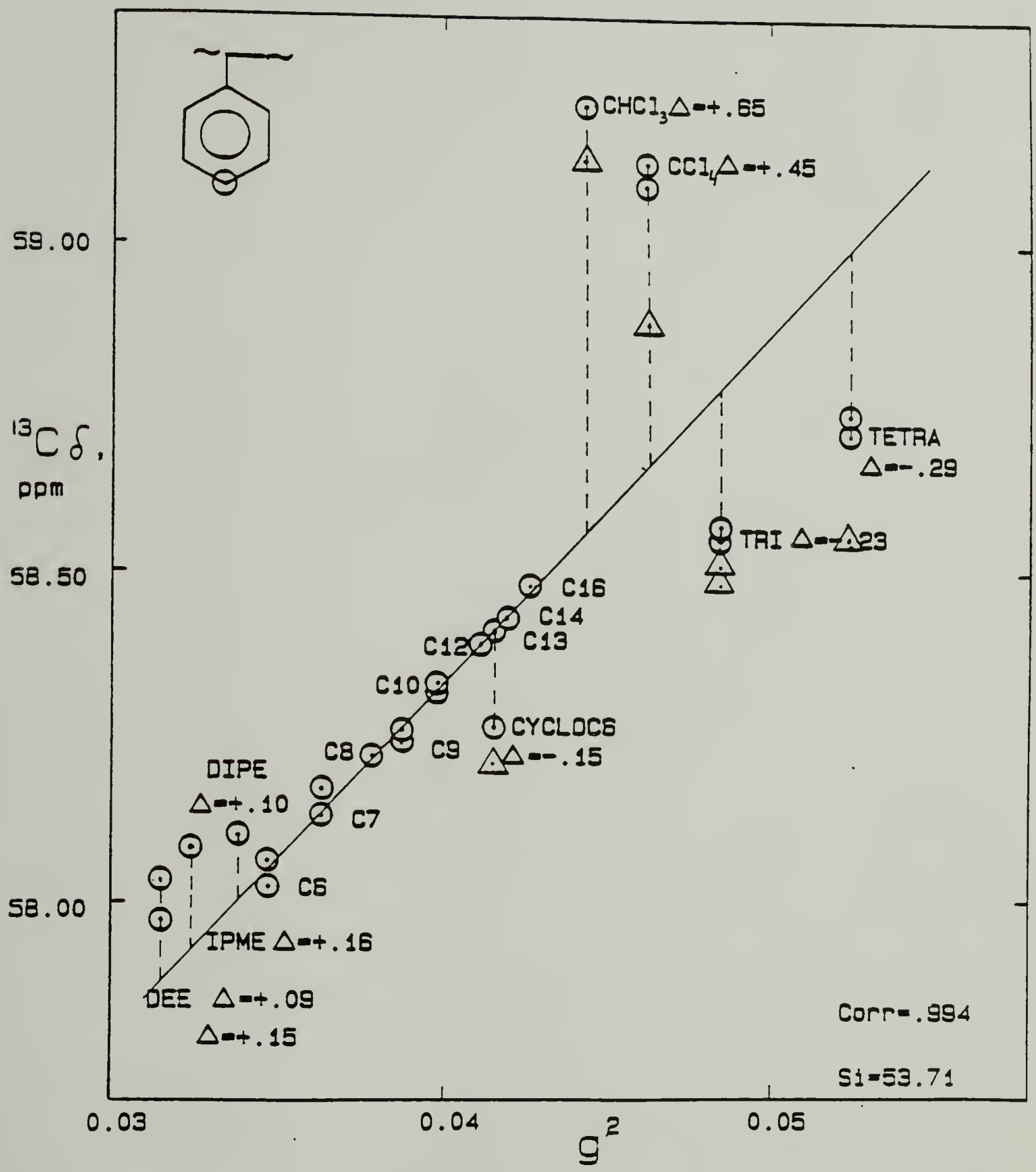

CHCl3 Δ=+.65
CCl4 Δ=+.45
59.00
13C δ, ppm
58.50
58.00
TETRA Δ=-.29
TRI Δ=-.23
C16
C14
C13
C12
C10
C8
C9
CYCLOC6 Δ=-.15
DIPE Δ=+.10
C7
C6
IPME Δ=+.16
DEE Δ=+.09
Δ=+.15
Corr=.994
Si=53.71
0.03
0.04
0.05
g2

Fig. VIII-11. Rummens plot of ^{13}C NMR chemical shifts for ortho and meta carbons in PS: (○) PS 600; (△) PS 17,500.

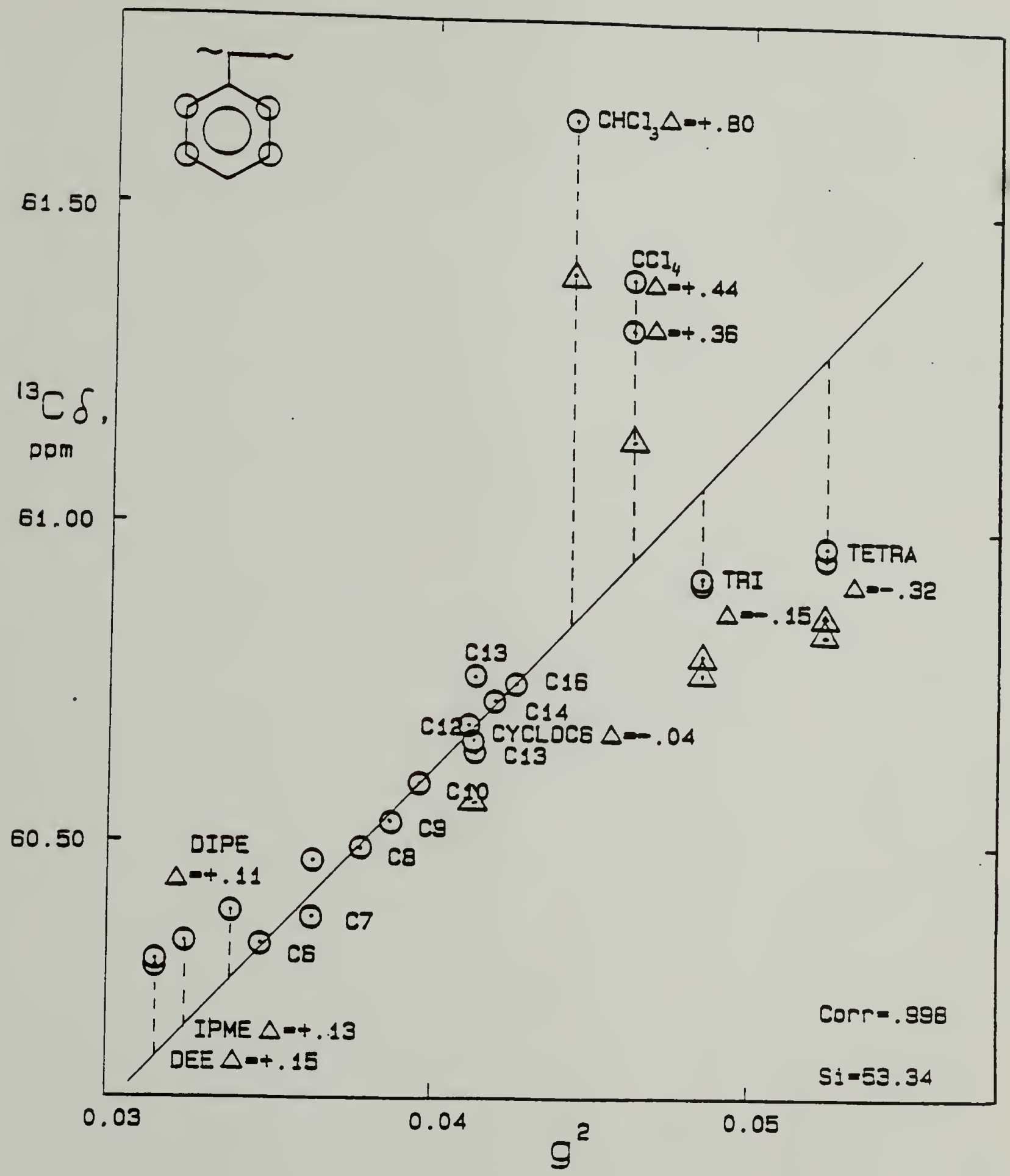

CHCl3 Δ=+.80
CCl4
Δ=+.44
Δ=+.36
TETRA
Δ=-.32
TRI
Δ=-.15
C13
C16
C14
C12
CYCLOC6 Δ=-.04
C13
C10
C9
C8
C7
C6
DIPE
Δ=+.11
IPME Δ=+.13
DEE Δ=+.15
Corr=.998
Si=53.34
61.50
61.00
60.50
13C δ, ppm
0.03
0.04
0.05
g2

Fig. VIII-12. Rummens plot of ^{13}C NMR chemical shifts for ipso carbon in PS: (○) PS 600; (△) PS 17,500.

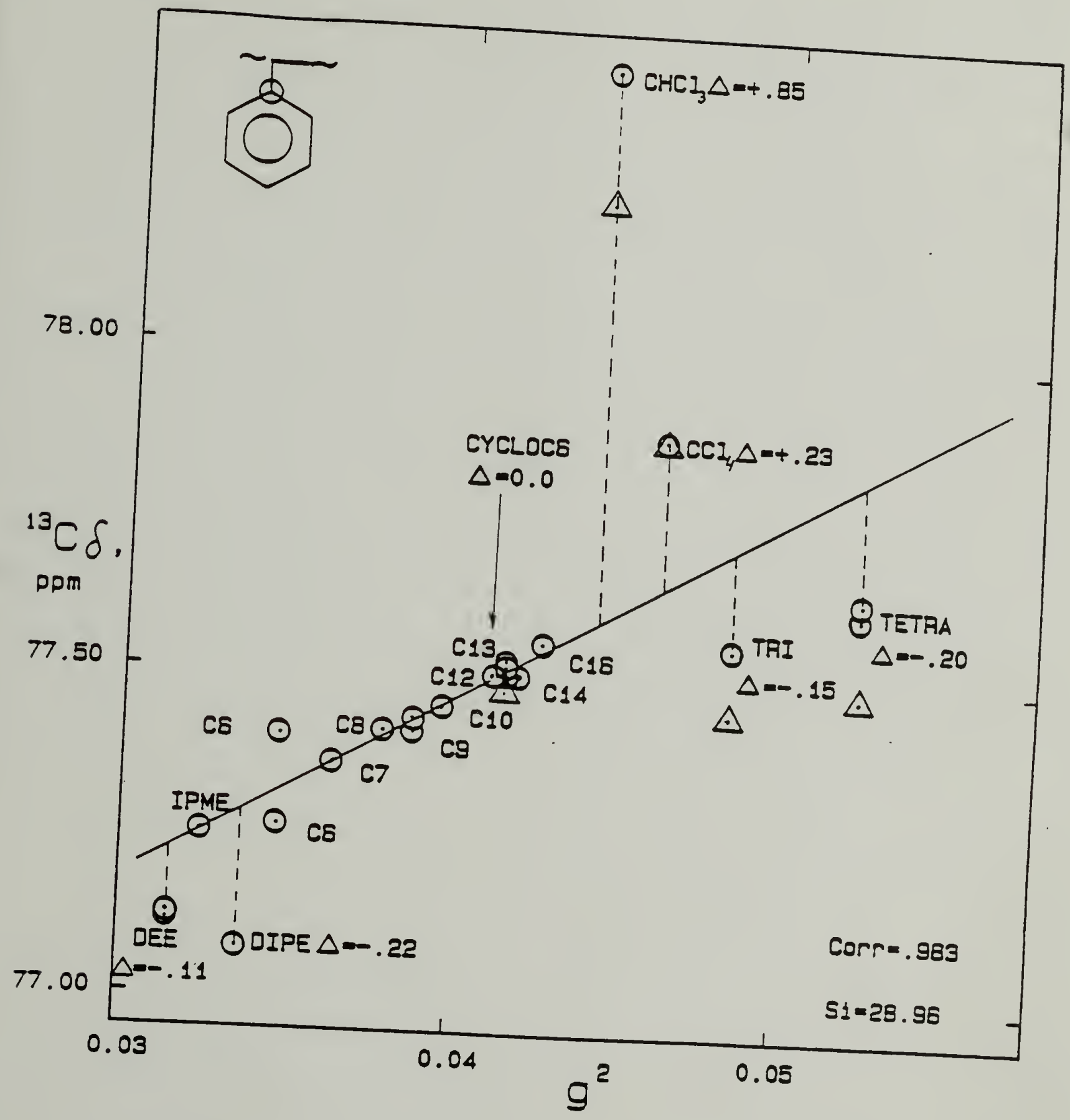

CHCl3 Δ=+.85
78.00
CYCLOC6
Δ=0.0
CCl4 Δ=+.23
13C δ,
ppm
77.50
C13
C12
C16
C14
C10
C9
C8
C7
C6
TRI
Δ=-.15
TETRA
Δ=-.20
IPME
C6
DEE
Δ=-.11
DIPE Δ=-.22
77.00
Corr=.983
Si=28.96
0.03
0.04
0.05
g2

Fig. VIII-13. Rummens plot of ^{13}C NMR chemical shifts for α carbon in PS: (○) PS 600.

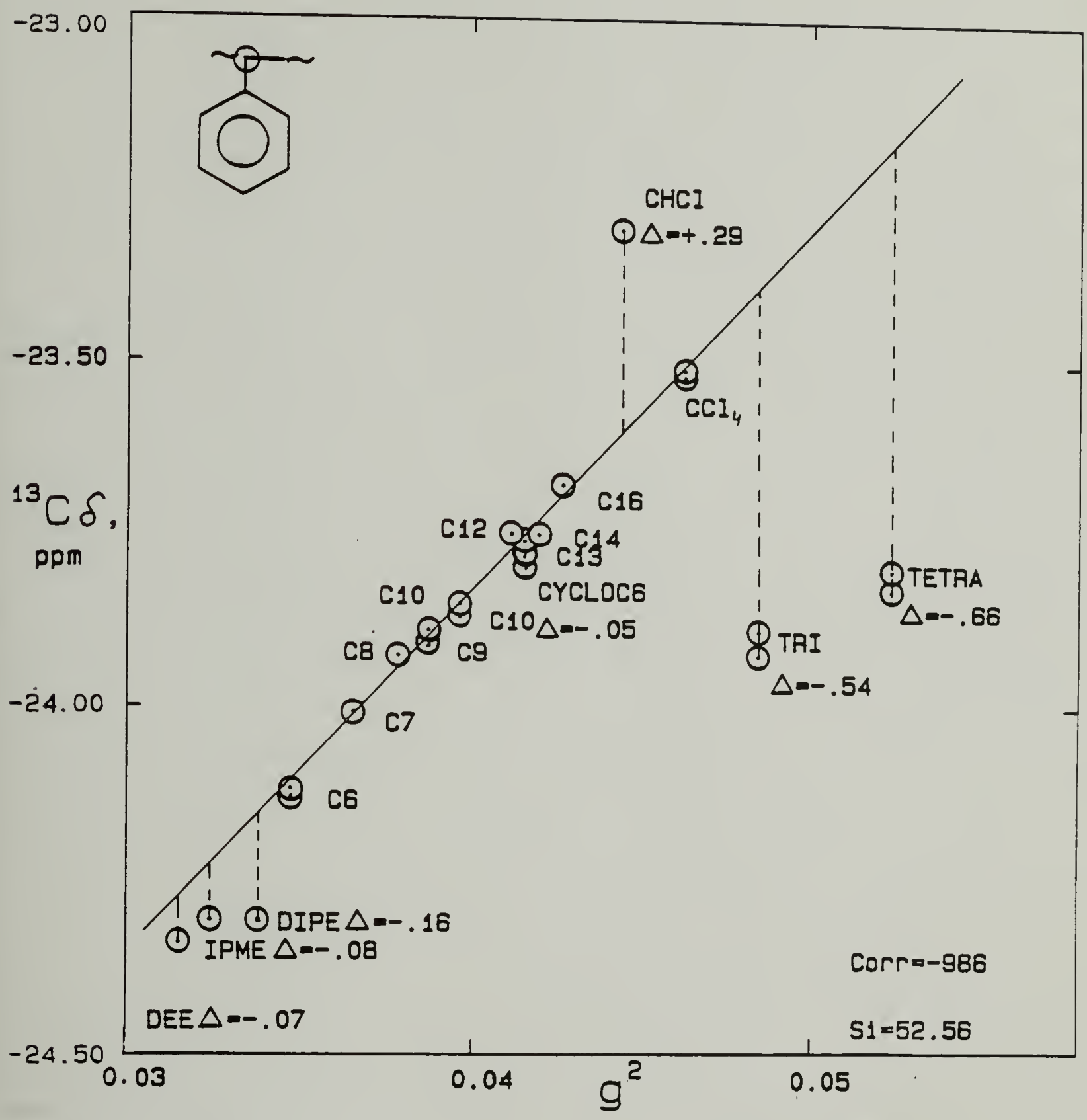
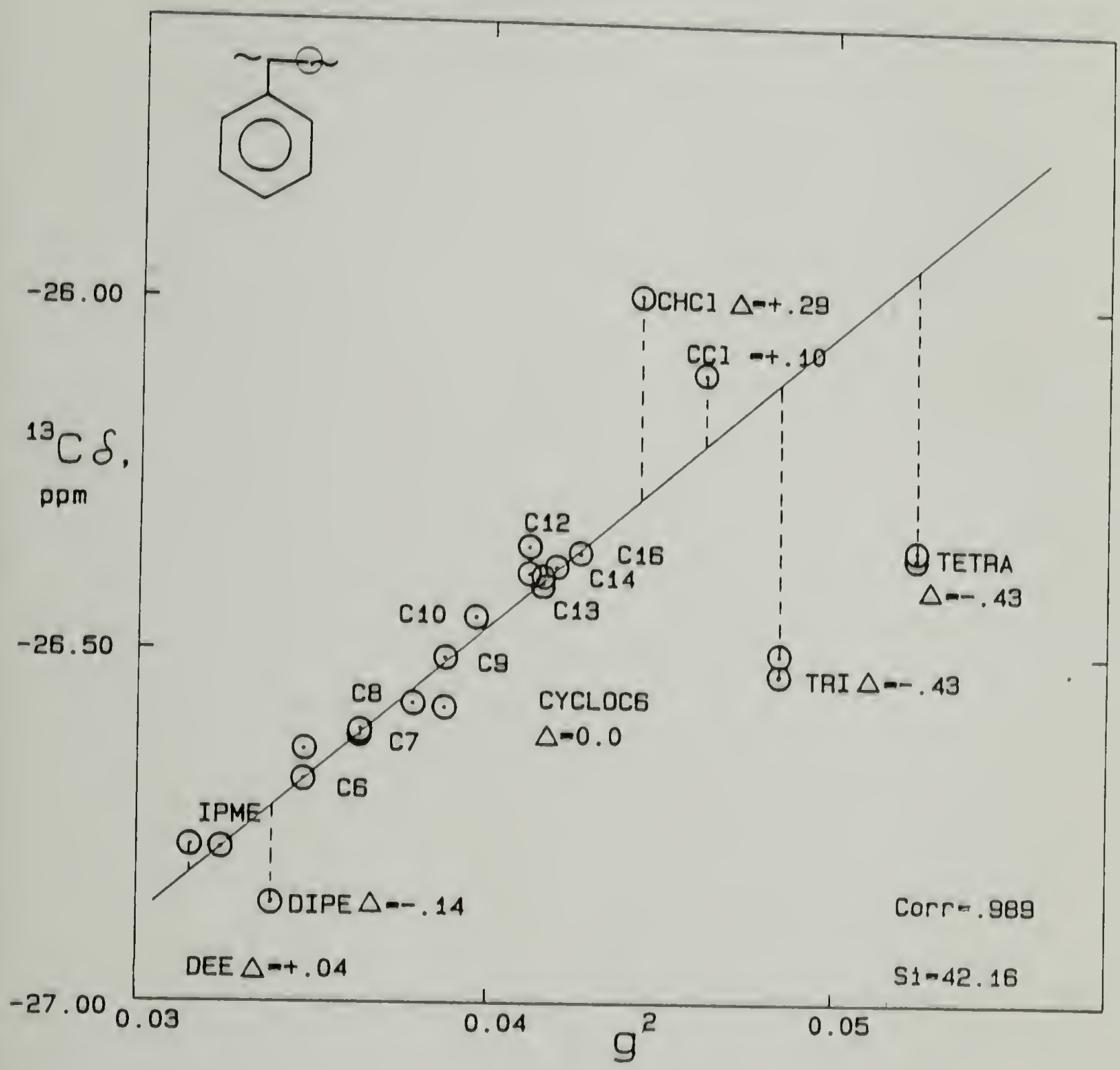

-23.00
-23.50
-24.00
-24.50
$^{13}C\delta$, ppm
0.03
0.04
0.05
g^2
CHCl
Δ=+.29
CCl_4
C16
C12
C14
C13
CYCLOC6
C10
C10 Δ=-.05
C8
C9
C7
C6
TRI
Δ=-.54
TETRA
Δ=-.66
DIPE Δ=-.16
IPME Δ=-.08
DEE Δ=-.07
Corr=-986
Si=52.56

Fig. VIII-14. Rummens plot of ^{13}C NMR chemical shifts for β carbon in PS: (○) PS 600; (△) PS 17,500.


-26.00
-26.50
-27.00
$^{13}C\ \delta$, ppm
CHCl Δ=+.29
CCl =+.10
TETRA Δ=-.43
TRI Δ=-.43
C12
C16
C14
C13
C10
C9
C8
C7
C6
CYCLOC6 Δ=0.0
IPME
DIPE Δ=-.14
DEE Δ=+.04
Corr=.989
S1=42.16
0.03
0.04
0.05
g^2

Slopes of van der Waals lines, Si, for all ring carbons of PS 600 are smaller than the corresponding values for cumene (Chapter VI, Table VI-5). It appears that this result may be explained by the Bovey's finding about the mutual position of the phenyl rings in isotactic PS (24). It was reported that phenyl rings partially "overlap" each other. Our findings indicate (Chapter VI) that the dispersive interaction of the cumene with n-alkanes consists of the interaction of ring hydrogens and the interaction involving π-orbitals. Since in PS the ring overlap hinders the access of n-alkanes to the ring it also reduces the intensity of the dispersive interaction and reduces the slopes of the van der Waals lines. The reduction is the strongest for the substituted ring carbon, 30%. Para carbon has the reduction of 10%. The Si for ortho and metha carbons shows a reduction of 7% from the average slope for the two carbons in cumene. This distribution of the reductions indicates that the main consequence of the ring overlap is the reduction in the intensity of the dispersive interaction between the n-alkanes and the π-orbital, relative to the case of cumene. This finding also suggests one general relationship in the polymer-solvent interaction. Apparently in the case of some polymers the polymeric structure itself does not allow for the full utilization of the structural characteristics of the repeat unit which may contribute positively to the IMI between the polymer and the solvent. CCl_4 induces deshielding of ring carbons of PS 600, the same as for cumene, indicating the same character of the interaction-charge transfer complex between the chlorine and the π-orbitals (25). The intensity

of the deshielding is also very similar. The substituted ring carbon is deshielded only 10% more and the para carbon 10% less than the corresponding carbons in cumene. Ortho and metha carbons are deshielded 30% stronger than average deshielding for the corresponding carbons in cumene. One possible explanation is that the molecule of CCl_4 must be tilted from the ring axis what results in a higher anisotropic deshielding of those two carbons. A zero deviation on the αCH and a negligible deshielding on βCH_2 indicate that those two groups do not have any specific IMI with CCl_4.

When PS 600 is dissolved in ethers it is possible to separate three groups of solvent-induced deviations from VDWL. Ortho and meta carbons and para carbons show weak deshieldings. The deshieldings induced by one ether are of similar intensities. The intensity of DIPE induced deshielding is similar, and the deshieldings induced by DEE and IPME are weaker than those they induce on cumene. Different from cumene, the substituted ring carbon in PS 600 is shielded when dissolved in DEE and in DIPE, and shows no deviation in IPME. The αCH show weak shielding with all three ethers while βCH_2 shows van der Waals interaction with DEE and IPME and a weak shielding with DIPE. This pattern of the deviations from VDWL may be explained if the π-hydrogen bond is assumed between the electron deficient hydrogens in ethers and the π-orbital in PS.

The access to the π-orbital is limited to only one direction: from para carbon toward the center of the ring. In addition, the axis of the alkyl segment has only a small angle toward the ring plane. In

this position the substituted ring carbon αCH and βCH_2 groups may be at the axis of the C-C bond and thus anisotropically shielded. In the case of the solutions in IPME, which interacts preferably with the OCH_3 group oriented toward the center of the π-orbital, the anisotropic effect is seen only on the α carbon. It is induced by the IPME interacting with the ring in the adjacent repeat unit. Larger ethoxy group affects both the substituted carbon and the α carbon in an adjacent unit but does not affect the β carbon. DIPE can approach the π-orbital only with one of its βCH_2 groups. This group affects anisotropically the substituted carbon. The intensity of shielding is higher than the one induced by DEE. The reason is apparently in the lower angle between the βCH_2 group axis and the ring plane, which is in turn exposing the substituted carbon even more to the anisotropic effect. In this interaction the second C-C bond of the same isopropyl segment may have anisotropic effect on the adjacent αCH and βCH_2 of the PS chain.

^{13}C NMR spectra have also been analysed for PS with MW = 17,500 (PS 17,500). This sample obtained from Pressure Chemicals Co., has a narrow distribution of molecular weights. It cannot be dissolved in n-alkanes, so the Rummens plot cannot be constructed for it. In order to gain more insight into the mechanisms of the IMI, between this polymer and the solvents, chemical shifts for this polymer in several solvents (Table VIII-5) have been introduced in the Rummens plot for PS 600 (Figures VIII-10 to VIII-14). The difference between the actual chemical shifts for two different PS is an example of the effect of

Table VIII-5

^{13}C NMR Chemical Shifts for PS 17,500 in Different Solvents*

No	Solvent	g^2	δcorr				
			Ci	Co,m	Cp	C_α	C_β
1	C_6H_{12}	4.15	77.99	60.57	58.21	-22.98	-26.49
2	C_6H_6	5.17	77.91			-23.39	-26.81
3	C_6H_6	5.17	77.88			-23.30	-26.67
4	TOL	5.05	77.86				-26.68
5	m-XYL	5.13	77.67			-23.05	-26.67
6	m-XYL	5.13	77.61			-22.98	-26.69
7	CCl_4	4.62	78.18	61.13	58.85	-22.87	-26.27
8	CCl_4	4.62	78.22	61.10	58.84	-22.87	-26.19
9	CCl_4	4.62	78.23	61.14	58.87		-26.24
10	CCl_4	4.62	78.37		58.82		-26.21
11	$CHCl_3$	4.43	78.73	61.37	59.07	-22.89	-26.02
12	$CHCl_3$	4.43	78.73	61.40	59.13	-22.73	-26.08
13	C_2HCl_3	4.84			58.47	-23.46	-26.53
14	C_2HCl_3	4.84	77.94	60.79	58.50	-23.44	-26.54
15	C_2HCl_3	4.84	77.94	60.79	58.50	-23.44	-26.59
16	C_2Cl_4	5.24		60.83	58.54	-22.82	-26.48
17	C_2Cl_4	5.24		60.86	58.54	-22.86	-26.43
18	DPE	6.22	78.15			-22.65	-26.38
19	DPE	6.22	78.15			-22.64	-26.38

*All values at 31°C, relative to the external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

the macromolecular character of the solute on its solubility. Chemical shifts for αCH in PS 17,500 are considerably different from those of PS 600. This is apparently the consequence of the polymer configuration which is more pronounced with the higher MW. This difference prevents the comparison of the two values on the Rummens plot.

It is characteristic that in almost all other cases the chemical shift for PS 17,500 is upfield from the shift for the corresponding carbon in the oligomer. The only exceptions were few cases where there was no difference. In none of the cases PS 17,500 has the chemical shift downfield from that of PS 600. It may be noticed that the smallest difference between chemical shifts of PS 600 and PS 17,500 occurs in the cyclohexane solutions. The biggest differences are seen in the chloroform solutions. Among the PS carbons the most sensitive to the change of MW are the chemical shifts of ortho and meta carbons. Less sensitive are the substituted ring carbon and β carbon. This pattern of chemical shift dependence on MW suggests that in the solutions of PS 17,500 occur more interactions between the polymer's phenyl rings than in corresponding solutions of PS 600.

The fact that the small difference between the chemical shifts is seen in cyclohexane solution indicates that the intensity of this interaction must not be stronger than that of a dispersive interaction.

Carbons which are the most sensitive to the anisotropic effect of the neighboring phenyl ring are ortho, meta, carbons which are the most sensitive to the effect of the molecular weight, and para. This

suggests that the interaction causing this shielding occurs due to the overlap of two phenyl rings which can be positioned with parallel Ci-Cp axis and with opposed orientations. In such position the βCH_2 and substituted ring carbon will be exposed to a small or negligible anisotropic shielding. It may be assumed that this mechanism of interaction is characteristic for the cohesive interaction of PS.

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CHAPTER IX

SOLVENT EFFECT ON THE BLEND COMPATIBILITY OF POLY(VINYL METHYL ETHER) AND POLYSTYRENE

Introduction

Poly(vinyl methyl ether), PVME and polystyrene, PS, form compatible polymer blends from cosolutions in tetrachloroethylene, benzene, toluene (1) and xylene (2), which exhibit lower critical solution temperatures (2-5). Blends obtained from cosolutions in methylene chloride, chloroform and trichloroethylene are inhomogeneous at room temperature (1,2,6). Blends cast from trichloroethylene can, however, be annealed to a homogeneous blend which exhibits both upper and lower critical solution temperatures (6).

The effect of the solvent on the compatibility of PS and PVME has been analyzed in terms of thermodynamic properties (4,7,8). To understand this complex relationship better it would also be of interest to understand the specific intermolecular interactions, IMI, governing the compatibility on a molecular level.

In the course of the last several years, it was demonstrated that solvent-induced changes in NMR chemical shift, SIS, may provide detailed information about the character of IMI (9-17). Based on such an analysis, the solubility of PVME in benzene has been attributed to the π-hydrogen bond between the electron-deficient methoxy proton and the π orbital in benzene. In addition, dispersive (van der Waals,

London) interactions have been found between every C-H group in PVME and benzene (18). The same kinds of interactions are believed to lead to the compatibility of PVME and PS.

The aim of this work is to understand how the competition between the specific interactions in the ternary system affects the compatibility of the blends of PVME and PS prepared from the cosolutions. To attain this goal, an analysis of SIS has been applied to solutions of PVME in benzene, toluene and cumene and to solutions of both polymers in n-alkanes, diethyl ether, isopropyl methyl ether, diisopropyl ether, cyclohexane and chloroform.

Samples of PVME of low molecular weight and of styrene oligomer, PS, (Chapter VIII) have been applied. The ^{13}C NMR chemical shifts for PVME (Chapter VIII, Table VIII-3) and for PS (Chapter VIII, Table VIII-4) have been analyzed applying Rummens' plot (Figures VIII-1 to VIII-4 and VIII-6 to VIII-9). In addition, deviations from the van der Waals line, VDWL, for each carbon in the molecule are represented schematically in Figures IX-1 to IX-4. In the case of the β carbon in IPME only an average deviation is shown for the two stereoisomers.

Interactions in the Blend

As it can be seen in Figure IX-1, IPME causes weak deshielding of unsubstituted ring carbons in PS. Both the pattern and intensities of these deviations are similar to those caused by diethyl ether and diisopropyl ether (Figures VIII-6 to VIII-9). It is unlikely that ortho and para hydrogens from PS engage with equal intensities in

Fig. IX-1: Deviations from the VDWL for (a) PS in isopropyl methyl ether and (b) PVME in cumene.

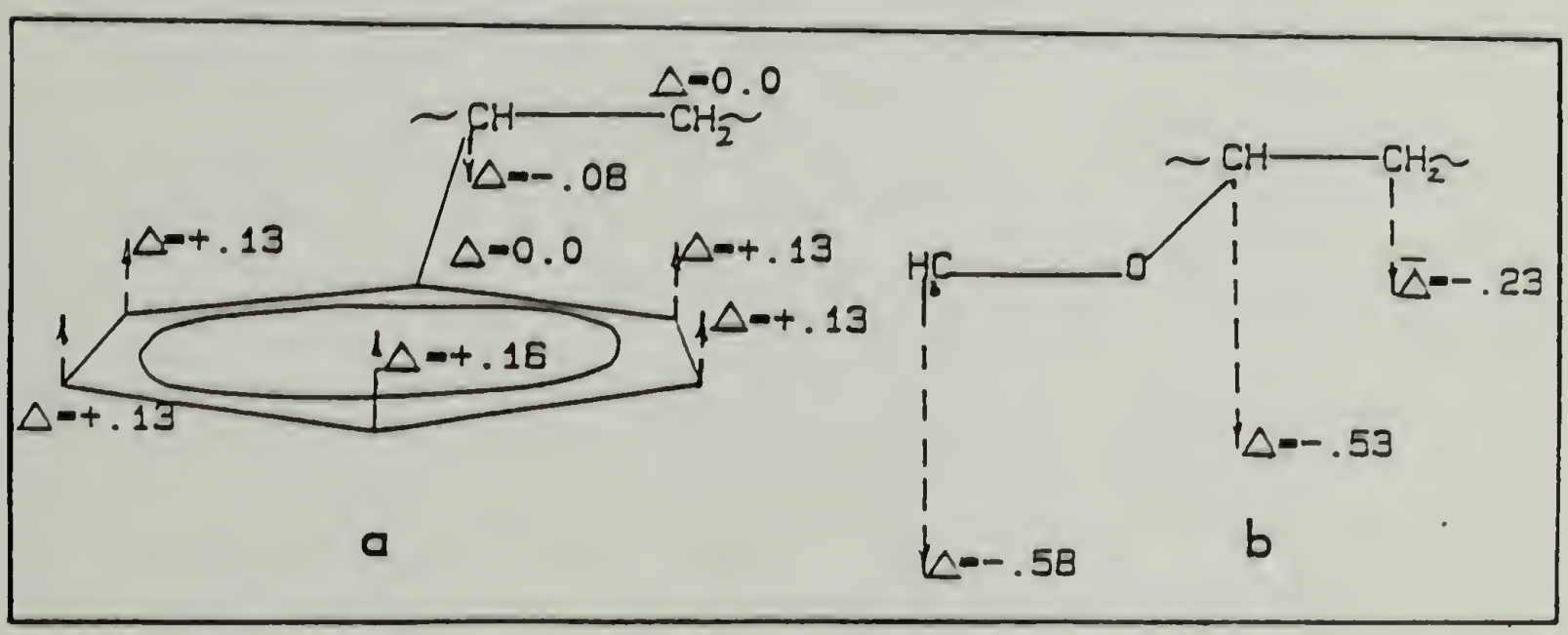

Δ=0.0
~CH—CH2~
Δ=-.08
Δ=+.13
Δ=0.0
Δ=+.13
Δ=+.13
Δ=+.16
Δ=+.13
a
~CH—CH2~
HC—O
Δ=-.23
Δ=-.53
Δ=-.58
b

Fig. IX-2: Deviations from VDWL for (a) PS and (b) PVME in cyclohexane.

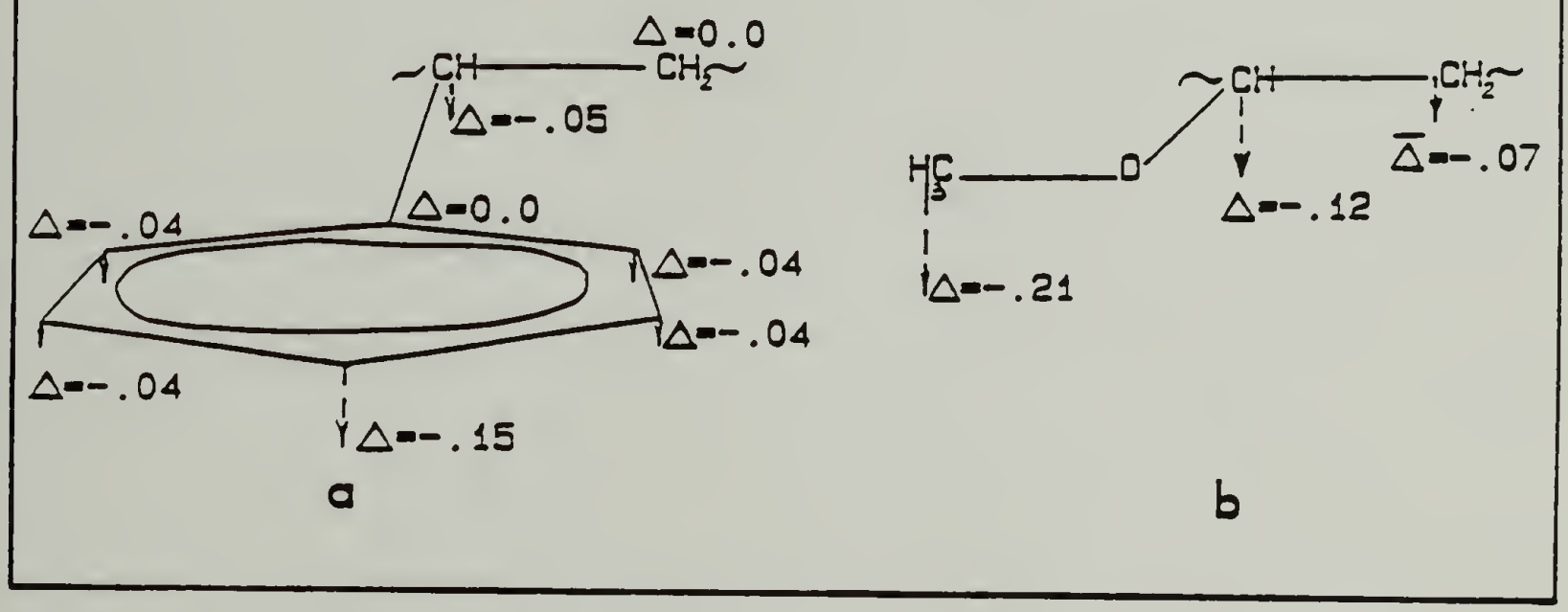

Δ=0.0
CH
CH2
Δ=-.05
Δ=-.04
Δ=0.0
Δ=-.04
Δ=-.04
Δ=-.04
Δ=-.15
a
CH
CH2
H3C
O
Δ=-.07
Δ=-.12
Δ=-.21
b

Fig. IX-3: Deviations from the VDWL for (a) cumene and (b) PVME in benzene and (c) benzene in isopropyl methyl ether.

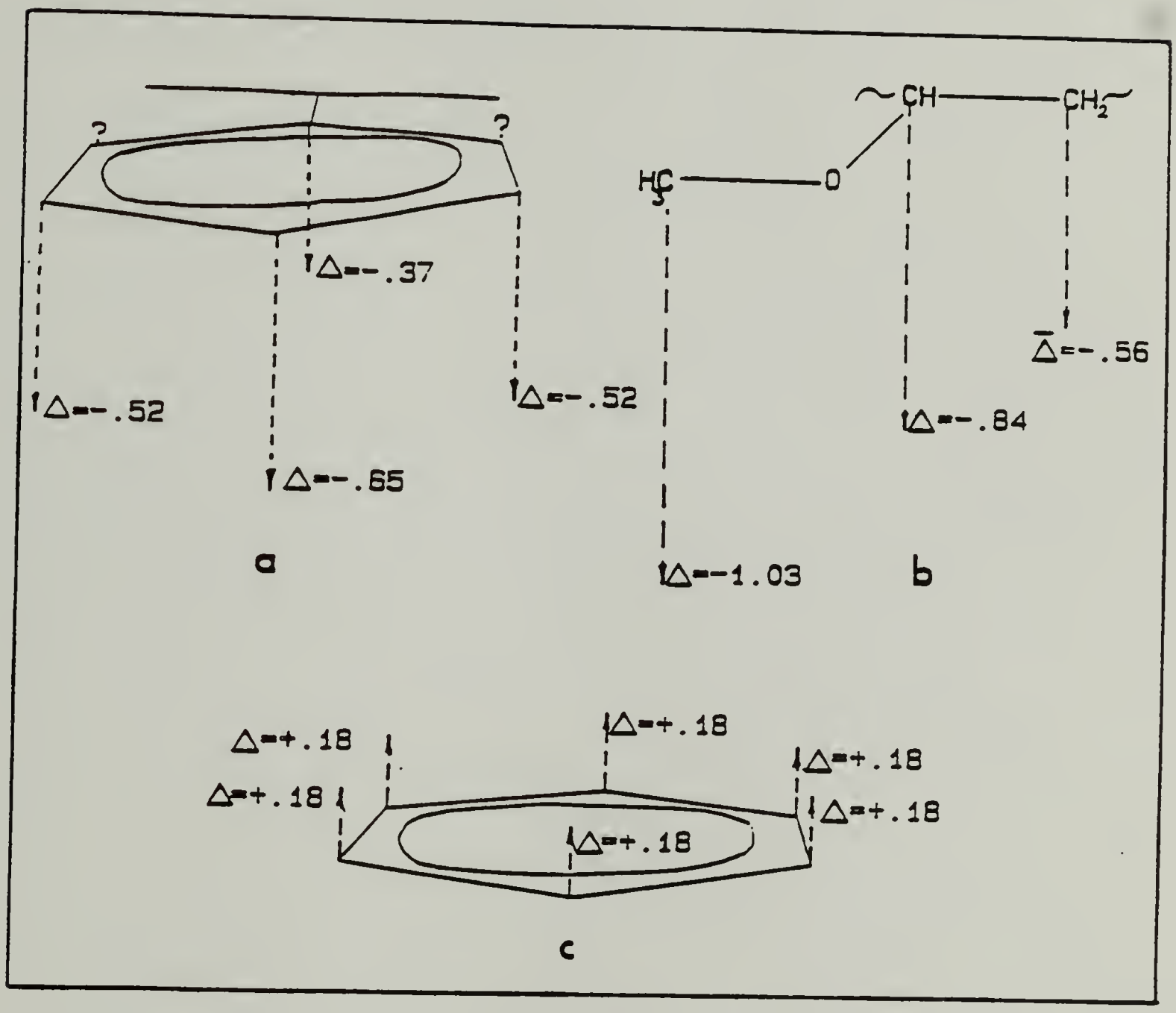
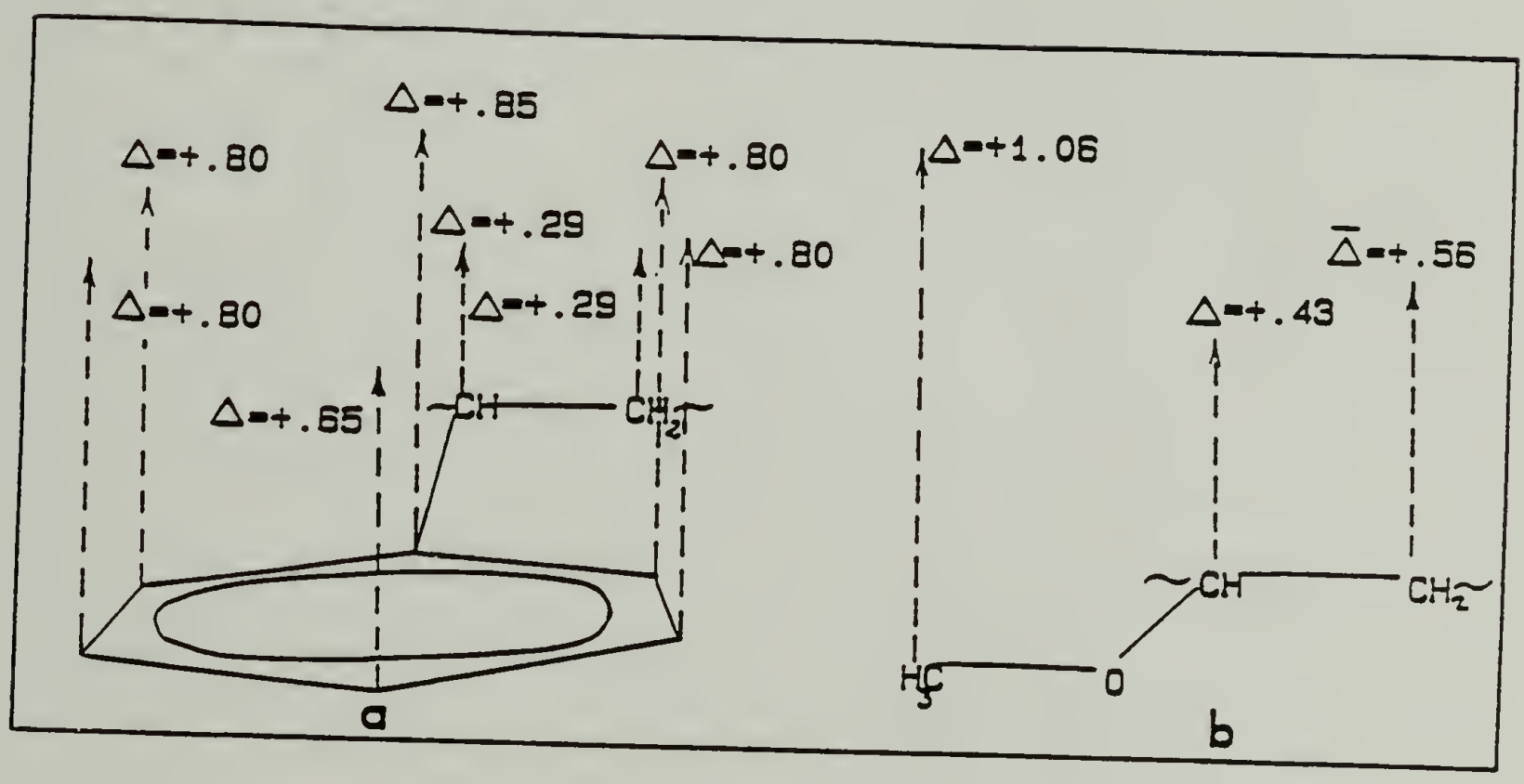

?
?
Δ=-.37
Δ=-.52
Δ=-.52
Δ=-.65
a
~CH
CH2~
H3C
O
Δ=-.56
Δ=-.84
Δ=-1.03
b
Δ=+.18
Δ=+.18
Δ=+.18
Δ=+.18
Δ=+.18
Δ=+.18
c

Fig. IX-4: Deviations from the VDWL for (a) PS and (b) PVME in chloroform.


Δ=+.85
Δ=+.80
Δ=+.80
Δ=+1.06
Δ=+.29
Δ=+.80
Δ=+.56
Δ=+.80
Δ=+.29
Δ=+.43
Δ=+.65
~CH
CH2~
~CH
CH2~
H3C
O
a
b

interactions with the ether oxygen. The observed pattern of deviations suggests interaction through the π-orbital. Low intensities of deviations for α methyne and β methylene carbons, however, suggest that those two groups do not have any specific interaction with IPME.

Cumene-induced deviations for PVME (Figure IX-1) indicate a strong anisotropic effect of the π orbital. By analogy with previous findings (18), it may be assumed that the methoxy group is involved in the π-hydrogen bond while other groups are involved in dispersive interactions.

Interactions in the Cosolution in Cyclohexane

Cyclohexane is a nonpolar compound which is believed to enter into dispersive interactions only (33). As solvent, it causes small upfield SIS which were attributed to the ring current (34). Both PS and PVME show weak upfield deviations from the VDWL (Figure IX-2). For PVME, the relative intensities of the deviations are 3.0:1.71:1.0; these resemble the relative ratios of the corresponding Si values (2.55:1.68:1.0). For PS all but the para carbons show only negligible deviations. Those results indicate that cyclohexane behaves as a dispersive solvent for both PS and PVME.

Cyclohexane-induced deviations from the VDWL are smaller than deviations in solutions used as models for the polymer blend. It may be deduced that mutual interaction between PS and PVME is stronger than interactions of any of the two polymers with cyclohexane. This

difference leads to preferred solvation and intimate mixing. The result is formation of a compatible polymer blend when the cosolution is dried. A cosolution of the two polymers (2.5 wt % PVME high molecular weight and 2.5 wt % PS 17,500) in cyclohexane forms, under different drying conditions, a transparent film.

Interactions in the Cosolution in Benzene or Toluene

PVME dissolved in benzene shows upfield deviations for all carbons (Figure IX-3). The pattern of the deviations indicates the same character of the interaction (18) as with cumene (Figure IX-1).

Chemical shifts for PS dissolved in benzene could not be identified correctly. As a model for this solution, one can observe deviations for cumene dissolved in benzene (18). Upfield anisotropic deviations occur for all ring carbons (Figure IX-3). It may be noticed that the substituted carbon in cumene, as well as the substituted carbon in mesitylene (18), shows considerable upfield deviations. This may suggest that cumene, mesitylene (and, presumably, PS) interact with benzene predominantly through parallel aromatic rings. This agrees with findings reported earlier (35).

Deviations from the VDWL, reflecting both the interaction and the anisotropy, do not allow one to determine whether benzene interacts more strongly with PS or with PVME. It was, however, reported earlier that the solubility parameters, χ, for PS and PVME in benzene are 0.26 and 0.15 respectively (7).

Benzene in IPME (Figure IX-3) shows deshielding for all carbons,

which are only a little stronger than those for PS dissolved in IPME. This indicates that the characteristics of the interaction of benzene and PS with IPME (or PVME) are similar. It may also be assumed that only a small difference exists between the energies of the interactions of the methoxy group in PVME and the phenyl group in PS with benzene. This will lead to an equilibrium between the methoxy groups interacting with benzene and those interacting with the phenyl ring in PS. As the concentration of the cosolution rises this equilibrium will shift more toward interaction among repeat units. This would lead toward more intimate mixing between PS and PVME and ultimately to a compatible blend (1,2).

PVME dissolved in toluene shows upfield deviations for all carbons with intensities similar to those induced by benzene (Figure 1). Cosolutions of PVME and PS in toluene yield compatible blends (1,2). Apparently the role of toluene is identical to that of benzene.

Interactions in the Cosolution in Chloroform

PS dissolved in chloroform, $CHCl_3$, shows very strong downfield deviations from the VDWL for all ring carbons (Figure IX-4). $CHCl_3$ dissolved in cumene shows deviations Δ = 0.38 ppm and Δ = 1.44 ppm in ^{13}C and ^{1}H NMR respectively (18). These results indicate a π-hydrogen bond between the phenyl ring in PS and $CHCl_3$. This agrees with published results (36,37).

The hydrogen bond between the electron-deficient hydrogen in $CHCl_3$ and the ether oxygen is usually considered a predominant mode of

IMI between $CHCl_3$ and ethers of low molecular weight (38). Results have been reported indicating the existence of more complex modes of interaction between those compounds (39,40). The second suggested mode of interaction is a charge transfer complex between chlorine and oxygen (33,41). $CHCl_3$ dissolved in IPME shows deviations of Δ = 0.65 ppm and Δ = 1.60 ppm in ^1H and ^{13}C NMR respectively (18). This indicates that $CHCl_3$ does act as a proton donor to ether but also that the $-CCl_3$ group is also significantly engaged in the interaction. PVME dissolved in $CHCl_3$ shows very strong downfield deviations for all carbons (Figure IX-4). The large difference between the deviations for methoxy and α methyne carbons, and the large deviation for the β methylene carbon indicate that interaction through the ether oxygen is not the only mode of interaction with $CHCl_3$. The pattern of the deviations suggests hydrogen bonding between electron-deficient hydrogens in PVME and chlorine in $CHCl_3$. The intensities of deviations (Figure IX-4) indicate that the interaction of PS with $CHCl_3$ is several times stronger than its interaction with IPME (Figure IX-1). Considering that deviations for PVME in cumene (Figure IX-1) are largely due to an anisotropic effect, one may conclude that PVME interacts much more strongly with $CHCl_3$ than with PS. From the ^{13}C NMR deviations for $CHCl_3$ induced by benzene (Δ = 0.38 ppm) and by IPME (Δ = + 1.60 ppm) it may be concluded that $CHCl_3$ interacts more strongly with PVME than with PS. This is in agreement with the values reported for the interaction parameters for the two polymers in $CHCl_3$ (χ = 0.13 and χ = -0.92 for PS and PVME respectively) (7).

Apparently strong interactions between polymers and solvent prevent the interaction between the repeat units of the two polymers in cosolution. As the concentration of the cosolution increases, PS, which has a poorer solubility in $CHCl_3$ (7), separates in a new PS-rich phase. Such a two-phase solution will result in an inhomogeneous blend (1,2).

In the cosolution of PVME and PS in $CHCl_3$, the solvent affects the formation of a homogeneous blend in two ways. Firstly it prevents the interaction among repeat units of the two polymers. In addition, different intensities of the interactions between two polymers and the solvent predetermine that they will reach critical concentrations at different cosolution concentrations. At present it is not possible to determine the relative importance of these two solvent effects.

Interactions in the Cosolution in Trichloroethylene

Interaction of trichloroethylene, C_2HCl_3, with aromatic solvents has been demonstrated by the change of NMR chemical shifts of C_2HCl_3 (42) and by the change of UV spectrum of the interacting benzene (43). In both cases the mode of the interaction was described as a π-hydrogen bond with C_2HCl_3 as proton donor (42,43). We have also demonstrated the formation of the π-hydrogen bond between C_2HCl_3 and aromatic compounds of low molecular weight (see Chapter VI). Aromatic solvents induce a very strong deshielding of the hydrogen and CCl_2 carbon, and weak deshielding of the CHCl carbon. This was interpreted as the engagement of hydrogen in the π-hydrogen bond whose

electrostatic effect causes the polarization of the double bond and shielding of the farer CCl_2 carbon.

C_2HCl_3 as solvent induces shielding for all but the alkyl substituted ring carbons in aromatic solutes (see Chapter VI, Table VI-4). We have demonstrated before that weak shielding of the unsubstituted, and the deshielding of the substituted ring carbons may also be associated with the π-hydrogen bond. In the case of C_2HCl_3 the small deshielding has been interpreted as the indicator for a π-hydrogen bond which is weaker than the bond built by chloroform, $CHCl_3$ (see Chapter VI).

PS dissolved in C_2HCl_3 shows shielding for all ring carbons (see Table VIII-4). The most important difference from the C_2HCl_3 induced deviations on cumene is the weak shielding (-0.15 ppm) of the substituted carbon. This may be interpreted as an indication of a π-hydrogen bond which is weaker than that between C_2HCl_3 and cumene. Considering that the access to π-orbitals in PS may be considerably reduced due to ring-ring steric hindrance, this appears a plausible conclusion. The shieldings on more accessible meta and para carbons in PS is, however, the same as in cumene (-0.14 vs. -0.14 and -0.21 vs -0.22 ppm, respectively), which does not support the previous conclusion. A possible explanation may be that in PS, just due to ring-ring proximity, a molecule of C_2HCl_3 may be in some position relative to the substituted carbon which it will never have in the case of cumene. This in turn may affect this carbon's anisotropic shielding.

Interaction of C_2HCl_3 with ether is reportedly exothermic (44) due to the hydrogen bond engaging C_2HCl_3 as a proton donor (45). We have demonstrated (Chapter VI, Tables VI-2 and VI-3) that C_2HCl_3 dissolved in ethers forms hydrogen bonds as proton donor, while the π electrons concentrate near the dichloro substituted carbon. C_2HCl_3 as a solvent causes anisotropic shielding of all carbons in ethers, very much similar to the shieldings induced by tetrachloroethylene, C_2Cl_4, in which the anisotropic effect overpowers the effect of the bonding IMI on the chemical shift.

PVME dissolved in trichloroethylene shows dehsieldings of all carbons (Chapter VIII, Table VIII-3). Intensities are different than on the corresponding carbons in IPME and the changes in the intensities are parallel to the changes seen between PVME and IPME dissolved in C_2Cl_4. Deshielding of the methoxy group is reduced approximately 15%, suggesting the minor reduction in accessibility due to the chain interference. The shielding of β carbon in β methylene group is only a fraction of the shielding of β methyl group (-0.13 vs. -0.59 ppm) and this too may be attributed to the greatly reduced accessibility of this group for relatively large molecule of C_2HCl_3. Shielding of α carbon which correspond to the shieldings C_2HCl_3 induces on the most accessible nonpolar groups (see Chapter VI) represents a striking change from the zero deviation for α C in IPME. One possible explanation is that small molecules of IPME and C_2HCl_3 did not need to have any such mutual position which would induce any shielding on α C. This may change in the case of the polymer. The predominance of the

strong shielding reminding of purely anisotropic effect on the PVME dissolved in C_2HCl_3 suggests that the interaction between the polymer and C_2HCl_3 must be weak. It does not indicate, by itself, the presence of any specific interaction.

From the changes in the chemical shifts of C_2HCl_3 we may conclude that it does form the specific IMI with both PS and PVME. However, the anisotropic character of the deviations that C_2HCl_3 induces on the two polymers prevents any estimate of the intensities of those IMI. From the already published results (45) and from our experiments we have estimated that the interaction is stronger with ethers than with aromatic compounds. This conclusion is in agreement with the published values for the solubility parameters for PS and PVME in C_2HCl_3 (χ = 0.19 and χ = 0.26, respectively) (7). As mentioned already in the case of the cosolution of the two polymers in $CHCl_3$ the interaction between the polymers and the solvent prevent the interactions between the repeating units of the two polymers while in cosolution. As the solvent is removed, PS which has a poorer solubility (7) separates to form a new phase and the further drying forms a two-phase blend (1,2).

Interactions in the Cosolution in Tetrachloroethylene

It has been suggested that aromatic compounds interact with C_2Cl_4 through a charge-transfer complex (46). UV spectra of benzene which is codissolved with C_2Cl_4 in an inert solvent did not however show the change characteristic for this kind of interaction (43).

PS dissolved in C_2Cl_4 shows shielding of all its carbons (see Table VIII-4 and Figures VIII-10 to VIII-14). The deviations are of considerable intensity for aliphatic, backbone, carbons (-0.63 ppm for α C and -0.42 ppm for β C). The deviation on α C corresponds to the maximal shieldings induced by C_2Cl_4. This intensity has been associated with the maximal anisotropic effect of C_2Cl_4 on very accessible and not very polarized molecules. Since β C cannot be polarized the smaller deviation probably indicate a steric hindrance.

Shielding of PS ring carbons reminds, by the distribution of intensities, to the shielding of corresponding carbons of cumene. Intensities are at average 0.10 ppm (25 - 30%) weaker than that on cumene (see Chapter VI, Table VI-5). Both the uniform reduction of the anisotropic effect relative to that on cumene, and the loss of the difference between shifts for ortho and meta carbon suggest that the access of C_2Cl_4 to the PS ring is reduced relative to the access it has to the ring of cumene.

C_2Cl_4 dissolved in aromatic solvents shows strong upfield deviations. Those deviations are very sensitive to the presence of the ring substituents. The deviation induced by cumene is 75% and by mesitylene is only 65% of that induced by benzene (see Chapter VI, Table VI-1). Apparently, substituents on the ring pose the steric hindrance for the clustering of aromatic molecules around C_2Cl_4 and thus reduce their anisotropic effect (47). Large influence of sterical hindrance on the intensities of anisotropic deviations of both PS dissolved in C_2Cl_4 and of C_2Cl_4 dissolved in aromatic solvents

suggests a very weak interactions.

Substituted carbons in PS, cumene and mesitylene show a deshielding which is somewhat smaller than on the unsbustituted carbons. This may represent the resultant of the anisotropic shielding and the interaction induced deshielding. This deshielding is understood by us as an indication that the π-orbital is engaged in the interaction (see Chapter VI) and it may be associated with the existence of a charge transfer complex (see Chapter V). The estimate of the intensity of the deshieldings induced by C_2Cl_4, indicates however that they are only the fraction of the deshielding induced by $CHCl_3$. If the charge transfer complex does exist it must be very weak. This does agree with the published reports that energy of interaction of some charge transfer complexes may be of the same order of magnitude as in van der Waals interactions. For the interaction of C_2Cl_4 with ethers the suggested mechanism was also a charge transfer complex (41). C_2Cl_4 dissolved in monofunctional aliphatic ethers shows however weak deshieldings (see Chapter VI, Table VI-1) which suggest that C_2Cl_4 is engaged as an electron donor. In addition those dehsielding are sharply reduced if the access to the ether's most electron deficient hydrogen is sterically hindered. Together with small deviations this suggests very weak interaction. PVME dissolved in C_2Cl_4 shows shieldings for all carbons (see Table VIII-3 and Figures VIII-6 to VIII-9). For methoxy and α carbon the intensity corresponds to that of more accessible carbons in ethers of small molecular weights (see Tables VI-1 to VI-3). The small average

shielding of β carbons may be explained only by the very reduced access of C_2Cl_4 to the β CH_2 group. The reason is much clearer when the relative sizes of C_2Cl_4 molecule and the repeat unit of PVME are considered. The shielding of methoxy group in PVME is ~ 12% reduced relative to the shielding of the same group in IPME. This may also be attributed only to the reduced accessibility of the group attached to the chain. However the degree of the reduction is not significant and it indicates that, as far as the interaction with C_2Cl_4 is concerned, methoxy groups in PVME has preserved the same character it has in IPME.

The only explanation for a considerably larger shielding of α C in PVME than in IPME (-0.55 vs. -0.26 ppm) may be that α H may be sheltered from the interaction by β CH_3 groups to a larger degree than by β CH_2 groups. Assuming that the difference between the maximal recorded shielding by C_2Cl_4 and the shielding of the observed group may all be attributed to the deshielding induced by the specific interaction, the estimated shielding will be at a level (0.25 or 0.13 ppm) suggesting only a very weak interaction. Findings that interactions of both PVME and PS with C_2Cl_4 are weak agree with the reported values for the solubility parameters of the two polymers in C_2Cl_4 (χ = 0.34 and χ = 0.36 for PVME and PS respectively (7)).

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CHAPTER X

INTERMOLECULAR INTERACTIONS OF LOW MOLECULAR WEIGHT ANALOGUES FOR COMPATIBLE BLENDS OF POLYSTYRENE AND POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

Introduction

Polystyrene, PS, and poly(2,6-dimethyl-1,4-phenylene oxide), PPO, form a compatible blend. This blend can be prepared by melt mixing (1) and it has a negative excess volume of mixing (2). This suggests that a specially favorable steric arrangement is formed between the two polymers.

The viscoelastic (3) and mechanical properties of the blend (2,3,4) are considerably different from these of the pure polymers. Particularly interesting is that instead of the brittle failures characteristic for both of the pure polymers, the blend has ductile failure (4). This suggests very intimate mixing (5,6) and a large number of the sites of the intermolecular interaction IMI, per chain. Those secondary bonds can transfer the energy between the chains and dissipate the stress by their own breaking, before it accumulates and causes the breaking of the primary bond.

The mechanism of the IMI between PPO and PS has been analyzed by means of the IR and UV spectroscopies (7). The results have suggested the interaction between the phenyl rings of PS and phenylene rings of PPO. Results of the one reported solid state NMR study of the blend (6) do not explain its IMI.

In order to better understand the mechanism of the IMI between the PPO and PS, an analysis of solvent-induced changes in NMR chemical shifts has been made for several low molecular weight compounds and olygomers which may serve as models for the two polymers. The 2,6-dimethyl phenol, 2,6DMP, is selected as the principal model compound for PPO. Of particular interest for the study of the IMI of PPO are the two groups which exist both in the polymer and in the model. Those are the methyl group and the C-H group at the positions 3 and 5 from the hydroxy group. The electron withdrawing effect of the ether's oxygen can induce the polarization of C-H bonds in its hydrocarbon segment. When the oxygen is attached to the phenyl ring it changes the shape and the energy of the π-orbital (8) and induces the polarization of the ring's C-H bonds (9,10) It has been demonstrated earlier that methoxy group polarizes all C-H bonds on the ring (11-13) as well as the vinyl group attached to the ring (14,15). From this it may be expected that the methyl group on the ring will also be polarized. The information about the effect of the phenoxy group and, to that matter, about the effect of the two, para positioned, phenoxy groups on the charge distribution on the ring could not be found in the literature. The near-identical ^{13}C NMR chemical shifts from methyl groups in 2,6DMP and in PPO indicate that both their electron densities and their molecular environment are nearly equivalent. In order to understand how the electron withdrawing effect of the oxygen affects the IMI, the interactions have been also analyzed for the oxygen-free analog of 2,6DMP, the m-xylene (Chapter VI, Tables VI-7

and VI-8).

In order to assess the effect of the neighboring 2,6-dimethyl-phenylene groups on the IMI the SIS has been analyzed for the methyl group in the middle segment of 2,6DMP trimer. In order to understand the role of the PPO as electron donor in the interaction, one of the solvents applied in the study is diphenyl ether, DPE. All ethers are usually considered n-electron donors in the IMI (16). However, when oxygen is sterically hindered (17) or when it is attached to an electron withdrawing substituent, such as phenyl ring (18), the n-electron donating ability of the ether is greatly reduced. It has been reported already that DPE is a much weaker electron donor than diethylether, DEE (18) and that it is one of the poorest electron donors among ethers (19). Aromatic ethers (20) and DPE (7,19) can, also interact as π-electron donors. In order to detect the character of the interaction of the DPE its effects on the chemical shifts have been compared with the effects induced by some symetrical aliphatic ethers, DEE, di-n-butyl ether, DnBE, and diisopropyl ether, DIPE. The effect of the π-orbital in DPE on the interaction has been compared with the effects induced by diphenyl methane, DPM, a structural analog of DPE, having a neutral methylene group instead of oxygen.

The role of the PS in the IMI of the blend is analyzed by observing IMI of cumene (Chapter VI, Tables VI-5 and VI-6) and the styrene oligomer, PS 600 (Chapter VIII, Table VIII-4).

Results and Discussion

Cumene dissolved in symmetrical n-aliphatic ethers (Tables VI-5 and VI-6) shows the deshielding of all its ring carbons. The most deshielded is the substituted carbon. This has been interpreted as the indication of a π-hydrogen bond between the π-orbital of the cumene and electro-deficient hydrogens of the ether. The para carbon, which is bearing the most accessible hydrogen in cumene is the least deshielded. This suggests the cumene probably does not form any hydrogen bonds involving the ring hydrogen and the oxygen of the ether.

PS 600 (Table VIII-3) in aliphatic ethers shows some shielding of the substituted carbon which has been explained as the anisotropic effect of the ether alkyl group (Chapter VIII). Other ring carbons are deshielded, para carbon being the least so. The same as in the cumene this suggests the absence of any hydrogen bond between ring hydrogen and the oxygen in the ether.

Cumene, pure, or dissolved in benzene, shows shielding of all its carbons. The least sensitive to the anisotropic effect of the aromatic solvents is the substituted carbon. The shielding is, however, always stronger by benzene than by cumene. This suggests that isopropyl group prevents cumene from approaching all the carbons to the same small distance at which benzene can approach them. Effect of cumene as solvent is even weaker if the aromatic solute has any alkyl substituents (Chapter VI). This all suggests that only a fraction of the

aromatic molecules is engaged in the interaction so that their rings are mutually parallel. This fraction is apparently smaller if the rings are more substituted. It has been demonstrated already that the structure of PS 600 reduces the access of alliphatic ethers to the π-orbitals. It may be estimated that the access will be even more difficult for a substituted aromatic compound.

DPM induces a shielding of the substituted carbon in cumene which is almost twice the intensity of the shielding induced by cumene (-0.56 vs. -0.30 ppm respectively). It also induces the shielding of the substituted, and ortho and meta carbons in PS 600 (-0.29 and -0.26 ppm, respectively). (Chemical shifts for other carbons could not be identified). The DPM may oscillate between the two extreme conformations. In one ring axes are at two mutually orthogonal planes. The π-orbitals are then at maximal distance. In the other conformation ring axes are in the same plane, thus enclosing the two π-orbitals in the 115° space between the two rings. In neither of these two conformations can a ring of DMP approach the ring of the cumene (or PS) for a complete overlap.

If the two ring axes were in the same plane, any nucleus in the space enclosed by the two rings will be exposed to an anisotropic effect of two rings and it shielding would be higher than the one induced by benzene. As data for the substituted carbon of cumene indicate, this is apparently the case here.

If the two phenyl rings in DPM were to be in the "orthogonal conformation" any approach of one of the rings to the ring of the

solute (particularly PS) would require a very exact steric positioning. The interaction of DPM in this conformation with PS does not appear to be likely. In addition because of the opposite anisotropic effects of the two orthogonal rings the induced deviation should be weaker than the one induced by benzene. When cumene is dissolved in DPE shieldings of all its ring carbons are considerably stronger than the ones induced by the cumene itself. Most remarkable, however, is that the relative ratios of these increases are practically identical for all the unsubstituted ring carbons. They are 1.52:1.92:1.89:1.92 for ipso, ortho, meta and para carbon, respectively.

The shielding of the substituted ring carbon by DPE is virtually the same as the one induced by DPM (-0.38 vs -0.39 ppm, respectively). This suggests that oxygen in DPE does not play any role in the interaction of DPE and cumene. Since DPE may have the same conformational states as the DPM it is apparent that it interacts in the conformation which has the ring axes in the same plane. The increase of the intensity of shielding relative to the shielding by cumene is similar as for DPM, suggesting again that the character of the interaction is determined by the aromatic character of the DPE only. The intensity of shielding is probably only the consequence of the specific conformation of the two rings. At present not enough of the experimental results are available to indicate whether the interactions of cumene (and PS) with DPM or DPE are only dispersive or they have some specific character.

When 2,6DMP is dissolved in DIPE or DnBE (Table X-1) its methyl

TABLE X-1

^{13}C NMR Chemical Shift for 2,6-Dimethyl Phenol in Different Solvents*

No	Solvent	g^2	C1			C3,5			C2,6			C4			CH_3		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	84.64			60.66			54.57			52.27			-52.68		
2	C6	3.47	84.76			60.84			54.74			52.45			-52.42		
3	C7	3.63	84.82			60.91			54.76			52.51			-52.29		
4	C8	3.78	84.94			60.98			54.88			52.53			-52.11		
5	C9	3.87	84.93			61.09			54.87			52.67			-52.06		
6	C10	3.96				61.10			58.85			52.70			-51.98		
7	C16	4.26	85.12	**		61.34	**		55.04	**		52.90	**		-51.66	**	
8	CCl_4	4.62	85.22	85.14	0.08	61.74	61.55	0.19	55.96	55.19	0.77	53.44	53.10	0.34	-51.03	-51.30	0.27
9	OEE	3.15	85.56	84.25	1.31	60.51	60.41	0.10	56.16	54.56	1.60	51.80	51.38	0.42	-51.87	-52.75	0.88
10	DnBE	3.79				60.84	61.02	-0.18	56.28	54.84	1.44	52.24	52.60	-0.36	-51.46	-52.71	0.65
11	DIPE	3.38	85.34	84.72	0.62	60.57	60.39	0.18	56.43	54.66	1.77	52.05	51.74	0.31	-51.35	-52.53	1.18
12	EGDME	3.52	84.33	84.78	-0.45	60.82	60.84	-0.02	56.42	54.72	1.70	51.99	52.44	-0.45	-51.81	-52.39	0.58
13	p-DIOX	4.09	85.98	85.05	0.93	61.28	61.21	0.07	56.45	54.96	1.49	52.45	52.78	-0.33	-51.49	-51.83	0.34
14	C_6H_6	5.17	84.96	85.56	-0.60	61.09	61.91	-0.82	55.37	55.42	-0.05	52.70	53.43	-0.73	-52.08	-50.77	-1.31
15	CUM	5.05	85.07	85.50	-0.43	61.20	61.83	-0.63	55.38	55.37	-0.01	52.79	53.45	-0.56	-51.88	-50.89	-0.99
16	OPhE	6.22	85.27	86.05	-0.78	61.34	62.58	-1.24				52.95	54.05	-1.10	-51.48	-49.74	-1.74
17	ANIS	5.38	85.46	85.65	-0.19	61.38	62.04	-0.66	56.00	55.51	0.49	52.84	53.55	-0.71	-51.69	-50.56	-1.13
18	OPhM	6.18	85.25	86.03	-0.77				55.74	55.85	-0.11	53.06	54.03	-0.97	-51.57	-49.78	-1.79

*All values at 31°C, relative to the external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) C1: correlation 0.9970 for the equation $\delta = 83.17 + 47.01\ g^2$ (ppm); b) C3,5: correlation 0.9940 for the equation $\delta = 58.58 + 64.44\ g^2$ (ppm); c) C2,6: correlation 0.9709 for the equation $\delta = 53.23 + 42.46\ g^2$ (ppm); d) C4: correlation 0.9864 for the equation $\delta = -50.35 + 59.57\ g^2$ (ppm); e) CH_3: correlation 0.9986 for the equation $\delta = -55.85 + 98.29\ g^2$ (ppm)

carbons are always strongly deshielded, opposite to weak or negligible deshielding of the corresponding carbons in m-xylene. In DEE the difference is smaller but methyl carbon from 2,6DMP is deshielded more than the one from m-xylene. This suggests that methyl group in 2,6DMP is polarized and it forms hydrogen bonds with the oxygen in the ethers. Deviations from VDWL for ring carbons in 2,6DMP also show an IMI stronger than dispersive but the difference from m-xylene is not so large. When m-xylene is dissolved in benzene all its carbons and hydrogens are shielded (Chapter VI, Tables VI-7 and VI-8). Chemical shifts of m-xylene in series of n-hexadecane-benzene mixtures show a linear dependence of the volume fraction of benzene (Chapter VI, Table VI-9 and Figure VI-1). This indicates that benzene is only a van der Waals solvent for m-xylene, and that shieldings are purely anisotropic.

When 2,6DMP is dissolved in benzene (Table X-1) its carbons are shielded to approximately the same extent as carbons in m-xylene. However, chemical shifts of 2,6DMP in series of n-hexadecane-benzene mixtures (Table X-2, Figure X-1) show an excess chemical shift [21] for the methyl carbon and carbons at positions 3, 4 and 5. Chemical shifts for the last two carbons even level off at high concentrations of benzene. This indicates that benzene preferably solvates the corresponding hydrogens. This is probably the consequence of the -hydrogen bonds between these electron-deficient hydrogens and -orbital of benzene. The pattern of the deviation from VDWL for 2,6DMP dissolved in cumene is the same, only the deviations are

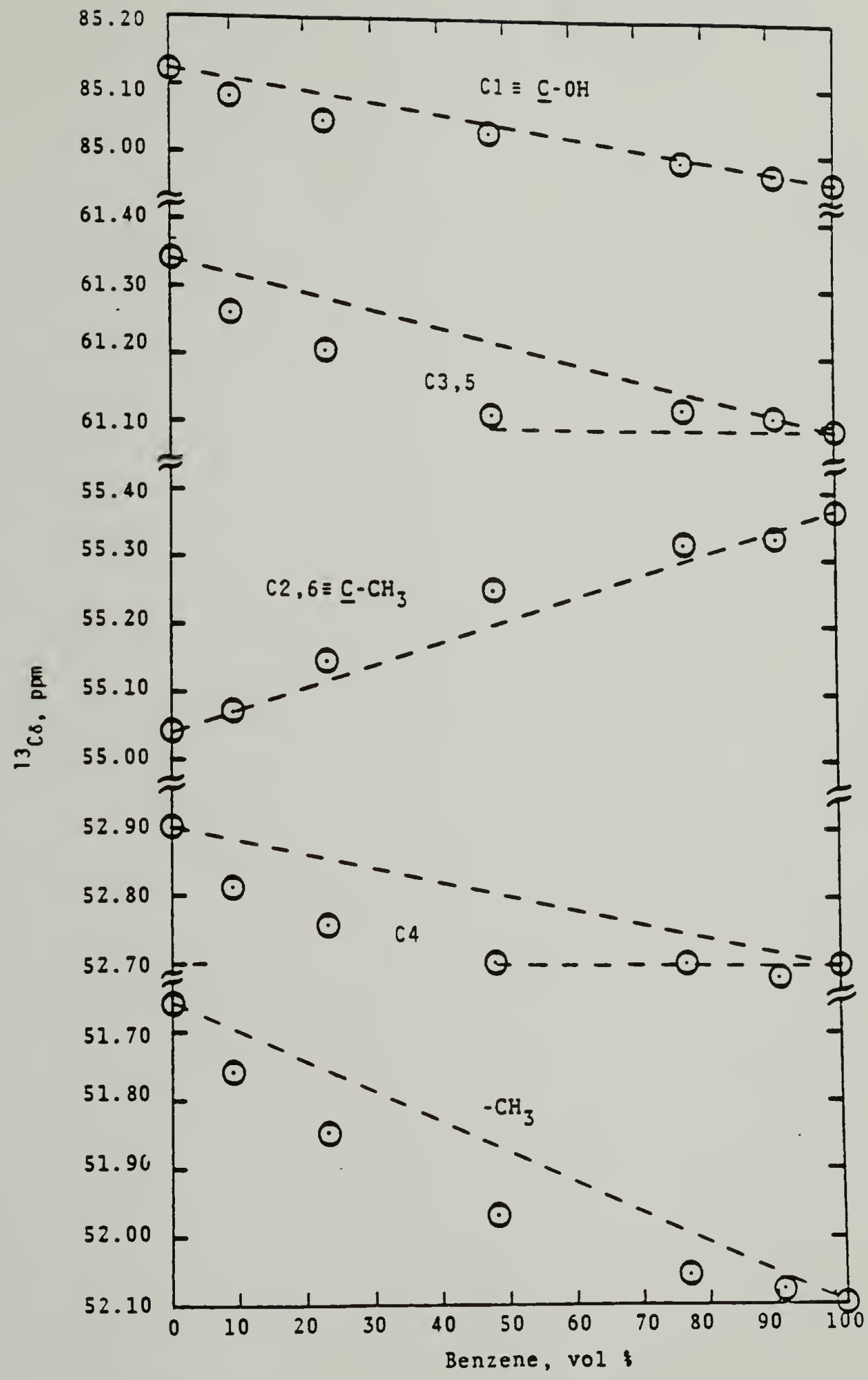
Table X-2

^{13}C NMR Chemical Shifts for 2,6-Dimethyl Phenol in Mixtures of n-Hexadecane and Benzene*

No.	Vol % C_6H_6	C1	C3,5	C2,6	C4	CH_3
1	0	85.12	61.34	55.04	52.90	-51.66
2	9	85.08	61.26	55.06	52.81	-51.76
3	23	85.06	61.21	55.15	52.76	-51.85
4	48	85.02	61.11	55.25	52.70	-51.97
5	77	84.99	61.12	55.32	52.70	-52.03
6	91	84.97	61.10	55.33	52.68	-52.06
7	100	84.96	61.09	55.37	52.70	-52.08

*All values at 31°C, relative to external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (Appendix, Table A-2).

Fig. X-1. The ^{13}C NMR chemical shifts for carbons of 2,6-dimethyl phenole in mixtures of n-hexadecane and benzene.


85.20
85.10
85.00
61.40
61.30
61.20
61.10
55.40
55.30
55.20
55.10
55.00
52.90
52.80
52.70
51.70
51.80
51.90
52.00
52.10
$^{13}C\delta$, ppm
C1 ≡ C-OH
C3,5
C2,6 ≡ C-CH$_3$
C4
-CH$_3$
0
10
20
30
40
50
60
70
80
90
100
Benzene, vol %

somewhat smaller.

When 2,6DMP is dissolved in benzene (or cumene) the most shielded is its methyl group. An apparent reason is its polarity and accessibility. Methyl group in 2,6DMP trimer (Table X-3) is also shielded by benzene, but the intensity of the shielding is only a half of that for methyl group in 2,6DMP. As discussed in Chapter VIII, for the case of PS, the presence of the adjacent repeat units represents a considerable steric hindrance for solvent molecules. This reduces both the intensity of the IMI and the accompanying anisotropic effect. In the spectra of 2,6DMP trimer chemical shifts for the carbons in positions 3 and 5 could not be successfully identified. However, the large reductions of the deviations for methyl carbons suggest that the IMI of the C-H bond at positions 3 and 5 can be disregarded. In analyzing the interaction mechanism of 2,6DMP with benzene (or cumene) it is important to pay attention to the SIS of the substituted ring carbons. As discussed in Chapter VI a certain fraction of the aromatic molecules may be in mutually parallel positions, thus inducing shielding of the substituted carbon. Methyl substituted carbons of the 2,6DMP dissolved in benzene and cumene shows only negligible deviations from VDML indicating the absence of any interaction involving parallel aromatic rings. This is opposing the finding reported earlier (7) that PPO and PS interact through the mutual interaction of their aromatic rings. The 2,6DMP dissolved in DMP or DPE show strong shielding of similar intensities. The ratio between the DPE-induced and cumene induced deviations for the same carbon is of the similar value,

Table X-3

^{13}C NMR Chemical Shifts for $-CH_3$ Carbon in the Middle Segment of 2,6-Dimethyl Phenol Trimer in Different Solvents*

No.	Solvent	g^2	δcorr	δVDWL	Δ
1	C7	3.63	-51.14		
2	C8	3.78	-51.06		
3	C9	3.87	-51.02		
4	C10	3.96	-50.98		
5	C13	4.15	-50.88		
6	C16	4.26	-50.83	**	
7	C_6H_6	5.17	-51.05	-50.39	-0.66
8	DPhM	6.18	-50.63	-49.90	-0.73
9	DPhE	6.22	-50.68	-49.88	-0.80

*All values at 31°C, relative to external standard (10 vol % p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). All symbols as in Appendix, Table A-1.

**Van der Waals line has the correlation 0.996 for the equation $\delta = -52.92 + 49.09\ g^2$ (ppm)

although not so uniform, as seen in the case of cumene.

As discussed earlier both DPM and DPE probably interact as aromatic compounds forming π-hydrogen bonds with electron deficient hydrogens in 2,6DMP. It may be also further deduced that IMI of this character are the probable mode of the cohesive IMI in the PPO.

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C H A P T E R XI

SOLUBILITY OF POLY(VINYL CHLORIDE) IN p-DIOXANE AND IN TETRAHYDROFURAN

Introduction

Although poly(vinyl chloride), PVC, is one of the most important commercially produced polymers, nothing has been published about the mechanism of its intermolecular interactions, IMI, with p-dioxane and tetrahydrofuran, THF.

Mixing of a low MW PVC analog 2,4-dichloropentane, 2,4DCP, with THF is exothermic (1) indicating the formation of specific IMI. There is no information on the thermodynamic changes associated with the dissolution of PVC, or any of its analogs, in p-dioxane.

Information about the IMI leading to the dissolution of PVC in the two cyclic ethers may be obtained from a Rummens-type (2) analysis of the NMR chemical shifts. Since PVC cannot be dissolved in n-alkanes, the analysis is performed on model compounds of low molecular weight. These are: 2-chloro propane, 2CP, which can be considered the monomeric model, and 2,4DCP, which, as a dimer, contains all the structural groups of PVC. In addition, effect of the solvent is analyzed for 2-chloro-2-methyl propane, TBC.

Results and Discussion

The TBC is an almost spherical molecule with nine equivalent hydrogens in its β methyl, βCH_3, groups. Chemical shifts for the

hydrogen of TBC (Table XI-1) have, in Rummens plot, a slope of the van der Waals line which is relatively small for an accessible nucleus (Si = 37.22 ppm). This suggests that its C-H bonds are not strongly polarized. Such conclusions are confirmed by the negligible deshiedling of the hydrogen in the pure compound. Apparently, TBC is a van der Waals liquid. The cyclic ethers, p-dioxane and THF, induce only a negligible deviation from VDWL indicating the absence of any hydrogen bonds or polar interactions.

The Rummens plot for ^1H chemical shifts of 2CP (Table XI-2) indicates similar Si for both the αCH and βCH_3 hydrogens (48.89 and 50.84 ppm, respectively). In the case of αCH the Si indicates a mildly polarized C-H bond. The Si for βCH_3 must be understood with regard to the results for TBC. It is probably a combination of weak polarization and the accessibility. Deviations from van der Waals line, VDWL, induced by the pure 2CP (Table XI-2) indicate that its cohesive interaction consists of the two IMI. One is the weak hydrogen bond between αCH and chlorine. The second, although it induces deshielding, is probably not a hydrogen bond but a dipolar interaction. The reason for this conclusion is that a C-H bond in βCH_3 cannot be expected to be more polarized than the analog bond in TBC.

When 2CP is dissolved in p-dioxane or in THF, the ^1H chemical shift for αCH cannot be identified. Chemical shift for βCH_3 indicates that both p-dioxane and THF act as van der Waals solvents. This is in agreement both with the finding for TBC and with the before mentioned

Tabel XI-1

^{1}H NMR Chemical Shifts for 2-Chloro-2-methylpentane in Different Solvents*

Solvent	g^2	δcorr	δVDWL	Δ
C6	3.47	-2.40		
C7	3.63	-2.34		
C10	3.96	-2.22		
C13	4.15	-2.14		
C16	4.26	-2.11	**	
TBC	3.60	-2.32	-2.35	0.03
p-DIOX	4.09	-2.19	-2.17	0.02
THF	3.89	-2.30	-2.24	0.06

*All values at 37°C, relative to external standard (benzene), corrected for diamagnetic susceptibility. Symbols as in Appendix, Table A-1.

**Van der Waals line has the correlation 0.9995 for the equation $\delta = -3.69 + 37.22\ g^2$ (ppm)

Table XI-2

^{1}H NMR Chemical Shifts for 2-Chloropropane in Different Solvents*

			αCH			βCH$_3$	
Solvent	g^2	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
C6	3.47	0.00			-2.60		
C7	3.63	0.05			-2.52		
C10	3.96	0.26			-2.36		
C13	4.15	0.36			-2.24		
C16	4.26	0.42	**		-2.21	**	
2CP	3.51	0.27	0.04	0.23	-2.42	-2.58	-0.16
p-DIOX	4.09		0.33		-2.19	-2.17	-0.02
THF	3.89		0.23		-2.41	-2.39	-0.02

*All values at 37°C, relative to external standard (benzene), corrected for diamagnetic susceptibility. Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) αCH: correlation 0.9879 for the equation $\delta = -1.68 + 48.89\ g^2$ (ppm); b) βCH$_3$: correlation 0.9990 for the equation $\delta = -4.37 + 50.84\ g^2$ (ppm)

conclusion about βCH_3.

In ^1H NMR the chemical shifts for 2,4DCP cannot be determined consistently. For this reason its interactions have been analyzed in the Rummens plot for ^{13}C NMR (Table XI-3). A ^{13}C spectrum for 2,4DCP has two peaks for each structural group, representing racemic and meso-isomer. Differences in the deviations from the VDWL for the two isomers are negligible, so the average values have been used for the analysis (Table XI-4).

It may be noticed that the cohesive interaction is characterized by a strong deshielding of the αCH carbon and by a negligible deviation for β methylene, βCH_2, carbon. This pattern of deviation suggests a moderate-to-strong hydrogen bond between α hydrogen and the chlorine. The hydrogen in β position may be engaged in the very weak hydrogen bond but its intensity depends on the diade configuration and it is relatively unimportant. This mode of the interaction may be traced back to the finding for the poor polarity of the βCH_3 bonds in 2CP and TBC. In addition, in the case of 2,4DCP, (and also of the PVC), if one α hydrogen is engaged in the hydrogen bond the access to the β hydrogen may be restricted only to certain directions. This is reflected in the weak shielding of β carbon in racemic 2,4DCP, and this reduces the probability of the interaction.

The 2,4DCP dissolved in p-dioxane and THF exhibits large deshielding of its α carbons. They have the same order of magnitude as in the cohesive interaction. This indicates that the two cyclic ethers are approximately as good electron donors for αH as is 2,4DCP

Table XI-3

^{13}C NMR Chemical Shifts for 2,4-Dichloro Pentane in Different Solvents

No	Solvent	g^2	CH_{rac}			CH_{meso}			CH_{2rac}			CH_{2meso}			CH_{3rac}			CH_{3meso}		
			δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ	δcorr	δVDWL	Δ
1	C5	3.24	-13.39			-14.47			-16.37			-16.96			-42.58			-43.65		
2	C7	3.63	-13.08			-14.49			-16.19			-16.78			-42.23			-43.30		
3	C10	3.96	-12.85			-13.99			-16.10			-16.68			-41.99			-43.09		
4	C13	4.15	-12.71			-13.79			-15.94			-16.57			-41.81			-42.86		
5	C16	4.26	-12.67	**		-13.75	**		-15.94	**		-16.55			-41.72			-42.80		
6	2,4DCP	3.51	-11.00	-12.52	1.52	-12.08	-13.61	1.53	-16.19	-15.85	-0.34	-16.38	-16.29	-0.09	-41.14	-41.57	0.43	-42.11	-42.65	0.54
7	p-DIOX	4.09	-10.93	-12.41	1.48	-12.19	-13.86	1.67	-17.02	-16.00	-1.02	-17.17	-16.61	-0.56	-42.24	-41.86	-0.38	-43.20	-42.94	-0.26
8	THF	3.89	-11.42	-12.91	1.49	-12.48	-14.01	1.53	-17.04	-16.09	-0.95	-17.04	-16.69	-0.35	-42.49	-42.03	-0.46	-43.07	-43.11	0.04

*All values at 31°C, relative to the external standard (10 vol% p-dioxane in D_2O), corrected for diamagnetic susceptibility (see Appendix, Table A-2). Symbols as in Appendix, Table A-1.

**Van der Waals lines have the following parameters: a) CH_{rac} correlation 0.9980 for the equation $\delta = -15.70 + 71.65\ g^2$ (ppm); b) CH_{meso}: correlation 0.9970 for the equation $\delta = -16.79 + 71.63\ g^2$ (ppm); c) CH_{2rac}: correlation 0.9870 for the equation $\delta = -17.77 + 43.15\ g^2$ (ppm); d) CH_{2meso}: correlation 0.9959 for the equation $\delta = -18.26 + 40.37\ g^2$ (ppm); e) CH_{3rac}: correlation 0.9993 for the equation $\delta = -45.28 + 83.49\ g^2$ (ppm); f) CH_{3meso}: correlation 0.9967 for the equation $\delta = -46.34 + 83.28\ g^2$ (ppm)

Table XI-4

Average Deviations from Van der Waals Line for 2,4-Dichloropentane in Different Solvents*

Solvent	αCH	βCH_2	CH_3
2,4 DCP	1.53	-0.22	0.49
p-DIOX	1.58	-0.79	-0.32
THF	1.51	-0.65	-0.21

*All values in ppm.

itself. However, 2,4DCP dissolved in ethers, exhibits also a moderate to strong shielding of its β carbons. The reason for the shielding is, as explained for pure 2,4DCP, in the reduced accessibility to β hydrogen after α hydrogen is already involved in a hydrogen bond. This limits the interaction of β hydrogens to the, shielding-inducing, colinear C-H···O hydrogen bond only. Apparently, the ether oxygen is either a better electro-donor than chlorine, or it is only more accessible. It is able to engage in moderate-to-strong hydrogen bonds with those hydrogens in 2,4DCP (and presumably in PVC) which cannot be engaged in the cohesive interaction. These additional hydrogen bonds allow for the dissolution of PVC in p-dioxane and THF.

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CHAPTER XII

SUGGESTIONS FOR FURTHER WORK

Our findings, reported here, together with the findings of other workers (1-3), demonstrate that the analysis of solvent-induced changes of NMR chemical shifts, SIS, is a versatile and useful method for the identification and study of the intermolecular interactions, IMI, in the solutions.

Although the method, as applied now, provides a lot of new, previously unavailable, informations, one may already envision several approaches for its improvement, and its use in new fields.

Instrumental Improvements

Already existing strong field ^{1}H NMR instruments have spectral resolution corresponding to the one currently obtained on routine ^{13}C spectra. Application of such instruments for SIS study might allow for complete separation of peaks for all chemically different hydrogens and the complete comparison of ^{1}H and ^{13}C SIS for every C-H bond in the analysed compound.

Nothing has been published to date on the interaction-induced changes in chemical shifts in high resolution solid state NMR. Although the Rummens approach cannot be applied in this case a comparison with results obtained from the low molecular weight and polymer solutions may provide crucial informations about the state of the IMI in the bulk polymer.

Broadening of the Scope

It has been demonstrated already that besides ^{1}H and ^{13}C also the ^{19}F (4) and ^{17}O NMR (5) show the SIS. Nothing has been published yet about ^{35}Cl chemical shift. Those five nuclei are principal elements for most of the polymers. Only ^{1}H and ^{13}C SIS have been analyzed by using Rummens approach. If it were applied on the first four, or eventually all five different nuclei, this would allow for a complete assessment of the role of every atom in the compound in the IMI. This will provide a more complete picture than the one obtained from ^{13}C NMR only.

Besides the chemical shift the IMI with the solvent can also affect the nuclear relaxation, coupling constants and nuclear Overhauser effect of a nuclei (6). The crosschecking of the SIS with nuclear relaxation times has been demonstrated to be very useful in analyzing the IMI (7). It may prove opportune to explore what improved information may be obtained by comparing the changes of these other parameters with SIS. One example may be the interaction of ethers with chloroform, analysed in Chapter III. The SIS data suggest the involvement of ether alkyl segments in the interaction, what is contradictory to the findings, based on different methods, by other workers (8). Nuclear relaxation experiments may provide additional information which will confirm, or deny, involvements of methyl and methylene segments in IMI. A similar comparison of SIS and nuclear relaxation data might help separate and eventually quantify the ani-

sotropic effect and IMI contributions to the SIS induced by aromatic solvents.

New Objects of Interest

The polymer-solvent IMI is an object of continuous interest. In order to improve the understanding of this IMI it is necessary to find how the slope of the van der Waals line, VDWL, and the solvent-induced deviation from VDWL depend on the temperature. It is further necessary to establish the precise relation between the deviation and the interaction enthalpy.

The change in the chemical shift appears to be very appropriate for the study of the phase separation process. Little has been published about the state of the IMI in the systems which exhibit the critical solution temperatures (9). It is also not known yet whether, between the spinodale and binodale, all the specific IMI, characteristics for the particular system are still existing (only the number of the interacting pairs being reduced proportionally). Another possibility is that certain IMI are first to be broken at spinodale and that the binodale represents the point where there is no more specific IMI. If the second is the case, can it be possible to define "subspinodales" for each of the several specific IMI existing in the system?

Some published results exist about the shift changes caused by the interaction of the two polymers in the cosolution (10). This problem merits more detailed analysis. The same is the case with the solu-

tions of the polymers in mixed solvents.

One polymer property which is very important for the long-range application is its IMI with oxygen molecule. The NMR spectroscopy appears to be a useful tool for the study of this field (11). It may be done by observing the change of the spectra for the polymer or model compound under oxygen-saturated conditions. The spectrum of the oxygen can be observed also while in the organic compound. It might be possible to distinguish the preferred sites for polymer-oxygen interaction. This will help understand the "pathway" of the oxygen diffusion through the polymer. One field related to this by both the nature of IMI and the method for its study is the study of the IMI between the oxygen and the perfluorinated organic compounds which are the substitutes for blood (12).

High Resolution Solid State NMR

In the solid state NMR a parallel observation may be performed of both the change in the chemical shift and the changes in relaxation times of nuclei involved in the interactions. Four groups of polymer properties can be analysed using this approach: crystalline structure, polymer orientation, polymer interaction with the absorbed compound of low molecular weight and polymer-polymer compatibility.

Crystalline structure. If a polymer can crystallize, specific and strong differences in the kind and/or intensity of intermolecular interaction should exist between the crystalline and amorphous phases.

It may be expected that the crystalline structure will exhibit a separate peak shifted from the peak for amorphous phase in the direction which will indicate the amount and extent of crystalline interaction. Such differences are reported for polyethylene but the analysis of the interaction has not been attempted (13). Relaxation properties should also be considerably different (14). By varying the degree of crystallinity and determining the degree of crystallinity using other methods, the change in the NMR signal could be correlated with, for example, x-ray or IR information on crystallinity.

Polymer orientation. Polymer orientation is a process controlled by intermolecular interactions. They must be strong enough to hold the polymer chain from recoiling under its internal stress. By comparing high resolution solid state NMR spectra for amorphous polymer with different degrees of orientation, it will likely be possible to identify exactly what intermolecular interactions control the oriented polymer. An analysis of the change in NMR spectra after annealing at different temperatures may also offer the information about the energy of these interactions.

An analysis of the orientation-induced changes in chemical shifts will also allow a better understanding of increases in content of crystallites on deformation. If the mechanical action generates an oriented amorphous state, then the orientation of the chain may be observed as a redistribution of the repeating units from the

completely random orientation toward certain drawn structures.

A large body of work has been performed on the solid state extrusion of amorphous and semicrystalline thermoplastics. Estimates of the degree of orientation have been made by x-ray, Fourier transform IR and birefringence. New information about the process will be obtained if the positive determination is made of the formation of the crystallites or of the the oriented amorphous phase and if the identification is made of the specific intermolecular interactions involved in the formation of oriented polymer by applying high resolution solid state NMR.

Interaction with absorbed compound. An analysis analogous to the study of SIS for polymer dissolved in a solvent of low molecular weight may be performed on polymer containing a small amount of the low molecular weight compound. This analysis may identify the mechanism of IMI which exists between the polymer and its plasticizer or which regulates the diffusion of the low molecular weight compound through polymer.

Polymer-polymer compatibility. Polymer-polymer compatibility is characterized by intermolecular interactions between the different components that are stronger than cohesive bonds within the pure components. The complete characterization of these phenomena thus requires study of all prominent cohesive interactions for each pure component and of all possible interactions between the two components.

The existence of the compatible polymer blends which show irreversible phase separations at critical solution temperatures (PS + PVME) (15) and PS + POClS (16) offers an opportunity to observe the destruction of the intermolecular interactions responsible for compatibility. The existence of blends that can be made compatible by melt blending (PPO with PS) implies rapid diffusion of polymer through polymer. It will be of great interest to observe the intermolecular interactions by high resolution solid state NMR between PPO and PS in the blends prepared by freeze drying of cosolution and by melt blending. Deviation of the chemical shift from the van der Waals values should be determined for different solvents featuring active sites which exist in the polymer. The difference in the shifts between the pure polymer and compatible or non-compatible blend may be interpreted as specific interactions. In the case of melt-blending, the compatibility at segmented levels will be seen as the complete engagement of the component of lower concentration. If this engagement is at the microdomain level, the interactions characteristic for the pure component may also be seen. In all cases, the change of relaxation times with the composition or with the state of blend will be determined and correlated with NMR shift deviations.

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CHAPTER XIII

NEW EMPIRICAL RELATION BETWEEN COHESION ENERGY DENSITY AND ONSAGER REACTION FIELD FOR SEVERAL CLASSES OF ORGANIC COMPOUNDS

Introduction

Cohesive energy density, CED (1), represents the cumulative strength of intermolecular interactions within a pure compound in the condensed state. An interest thus exists both in determining the contributions of each interaction type to the total CED and in correlating the CED with other material properties.

For compounds devoid of strong interactions, cohesive interactions may be considered to be the sum of dispersive (nonspecific) interaction (2), dipole-dipole (3) and dipole-induced dipole interactions (4,5). The contribution of each interaction type to the total CED may be estimated as the sum of interaction energies for pairs of molecules whose physical propeties, such as: dipole moment (6), polarizability (7) and ionization potential (8), are known. These approaches can be applied, however only as approximations (1). This subject has been reviewed by Hildenbrand and Scott (1), by Gardon (9) and by Pitzer (10). A review (11) is also available of the several approaches (12-14) for calculation of contributions to the CED of strong intermolecular interactions, such as hydrogen bonds.

Correlations between CED and other molecular properties are of double importance. They may permit an indirect determination of CED, and, more important, may help understand the mechanisms of interactions.

The refractive index, n (15), is one of several material parameters than can be correlated to other physical properties. Several efforts have been made to develop correlations (16-20) between CED and the Lorentz-Lorenz function (21). Generally attempts were made to correlate values for a broad array of compounds of different chemical types. Results apparently do not reveal any mechanism which would be common for the cohesive interactions of all the compounds.

Significant theoretical effort has been oriented toward understanding the relation between the evaporation enthalpy of organic compounds and the intensity of the Onsager reaction field, ORF (7,22-25)

$$\underset{\sim}{R} = \frac{2}{a^3} \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \underset{\sim}{\mu} \qquad \text{(XIII-1)}$$

(a is the diameter of Onsager's spherical cavity, enclosing the dipole moment, $\underset{\sim}{\mu}$, and ε is the bulk dielectric constant of the compound (22)). Theoretical results indicate a functional dependence of cohesive energy on ORF (7,23-25). However, the agreement between theoretically calculated and experimentally determined values has been only qualitative. A possible limitation in those theoretical approaches may be that a single relation was attempted for an array of unrelated and structurally dissimilar compounds.

To our knowledge, there has been no prior published attempts to correlate experimental values of CED (or quantities reflecting the intensity of cohesive interaction) with any of the parameters charac-

terizing the intensity of ORF for the range of homologous organic compounds.

Method

By introducing the Maxwell relation (26)

$$\varepsilon = n^2 \qquad \text{(XIII-2)}$$

(where $n = n_{D,25}$ is the refractive index of the compound for the Na D line (5992.6 Å) at 25°C (21)) the intensity of the ORF can be expressed as

$$\underset{\sim}{R} = \frac{2}{a^3}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\mu \qquad \text{(XIII-3)}$$

or

$$\underset{\sim}{R} = g\,\frac{2\mu}{a^3} \qquad \text{(XIII-3a)}$$

where the reaction field factor

$$g = \frac{n^2 - 1}{2n^2 + 1} \qquad \text{(XIII-4)}$$

is a dimensionless material parameter (7). It represents the effect of the continuum on the ORF induced by the permanent dipole embedded in it (22). It has been demonstrated earlier that expressions (3a) and (4) also apply to the intensity of ORF induced by the fluctuating dipole in a nonpolar compound (23).

CED for the compound can be calculated from the enthalpies of evaporation at the equilibrium vapor pressure at 25°C (9,27). The specific choice of the compounds whose characteristics were correlated in this analysis has been dictated by the availability of the reliable enthalpic data for the homologue series (9,27). Compounds selected have been classified in six homologous series (Table 1) and in at least three categories:

(a) n-alkanes, 1-n-alkenes and n-alkyl benzenes, that exhibit only dispersive interactions (1)

(b) ketones, that in addition exhibit dipolar interactions (1,28,29), and

(c) alcohols, that may further interact through hydrogen bonding (1,30).

Linear alkyl segments are present in every compound, their length being the difference between members in each series, and all of the compounds may be represented as a linear chain without a bulky side group. Compounds with different chemical properties, but with an equal number of atoms in the chain are homomorphous, similar in both shape and size. One example is the group n-hexane, 1-n-hexene, n-pentanol and 2-hexanone.

Results

Relations expressed in Table XIII-1 and in Fig. XIII-1 to Fig. XIII-3 indicate that within each homologous series, CED depends linearly on the single material parameter, g^2

TABLE XIII-1

Cohesion Energy Densities and the Onsager Reaction Field Parameters for Several Homologous Organic Series at 25°C and 1 atm.

No.	Compound	g^2	CED, cal/cm^3	Ref.
	n-alkanes - correlation coefficient[a] 0.9990			
1	propane	0.0235	40.96[b]	14
2	butane	0.0290	46.24[b]	14
3	pentane	0.0320	49.22	12
4	hexane	0.0343	52.80	12
5	heptane	0.0361	55.22	12
6	octane	0.0374	57.01	12
7	nonane	0.0385	58.79	12
8	decane	0.0394	59.63	12
9	undecane	0.0404	61.00[c]	13
10	dodecane	0.0411	62.73[c]	13
11	tetradecane	0.0419	63.20[c]	13
	1-alkenes - correlation coefficient 0.9988			
12	pentene	0.0338	49.18	12
13	hexene	0.0360	49.33[c]	12
14	heptene	0.0377	55.92	12
15	octene	0.0389	57.69	12
16	nonene	0.0399	59.10	12
17	decene	0.0407	60.24	12
	Methyl-n-alkyl ketones - correlation coefficient 0.9945			
18	2-propanone	0.0325	95.43	13
19	2-butanone	0.0351	85.93	13
20	2-pentanone	0.0367	79.57	13
21	2-hexanone	0.0381	74.30	13
22	2-heptanone	0.0394	72.25	13
23	2-octanone	0.0401	71.40[c]	13
	Benzene and alkyl substituted benzenes - correlation coefficient 0.9885			
24	benzene	0.0514	83.86	12
25	toluene	0.0509	79.43	12
26	ethylbenzene	0.0507	77.23	12
27	n-propylbenzene	0.0502	74.63	12

TABLE XIII-1,continued

No.	Compound	g^2	CED, cal/cm^3	Ref.
	Linear alcohols with odd number of carbons - correlation coefficient 0.9885			
28	methanol	0.0283	210.25	13
29	propanol	0.0359	141.61	- 13
30	pentanol	0.0391	118.81	13
31	heptanol	0.0411	100.00	13
	Linear alcohols with even number of carbons - correlation coefficient 0.999			
32	ethanol	0.0326	161.29	13
33	butanol	0.0377	129.96	13
34	hexanol	0.0403	114.49	13
35	octanol	0.0418	106.09	13

[a]Since not all conditions are know for the experimental determination of these material parameters, linear correlation coefficients were determined only for data from one source (as indicated by reference).

[b]Refractive index determined at different pressures and temperatures. Experimental conditions for the determination of CED are unknown. Points not considered in correlation.

[c]Points not considered in correlation.

Fig. XIII-1. Change of CED with g^2 for n-alkanes (○) and 1-n-alkenes (◒) at 25°C; superscripts correspond to those in Table XIII-1.

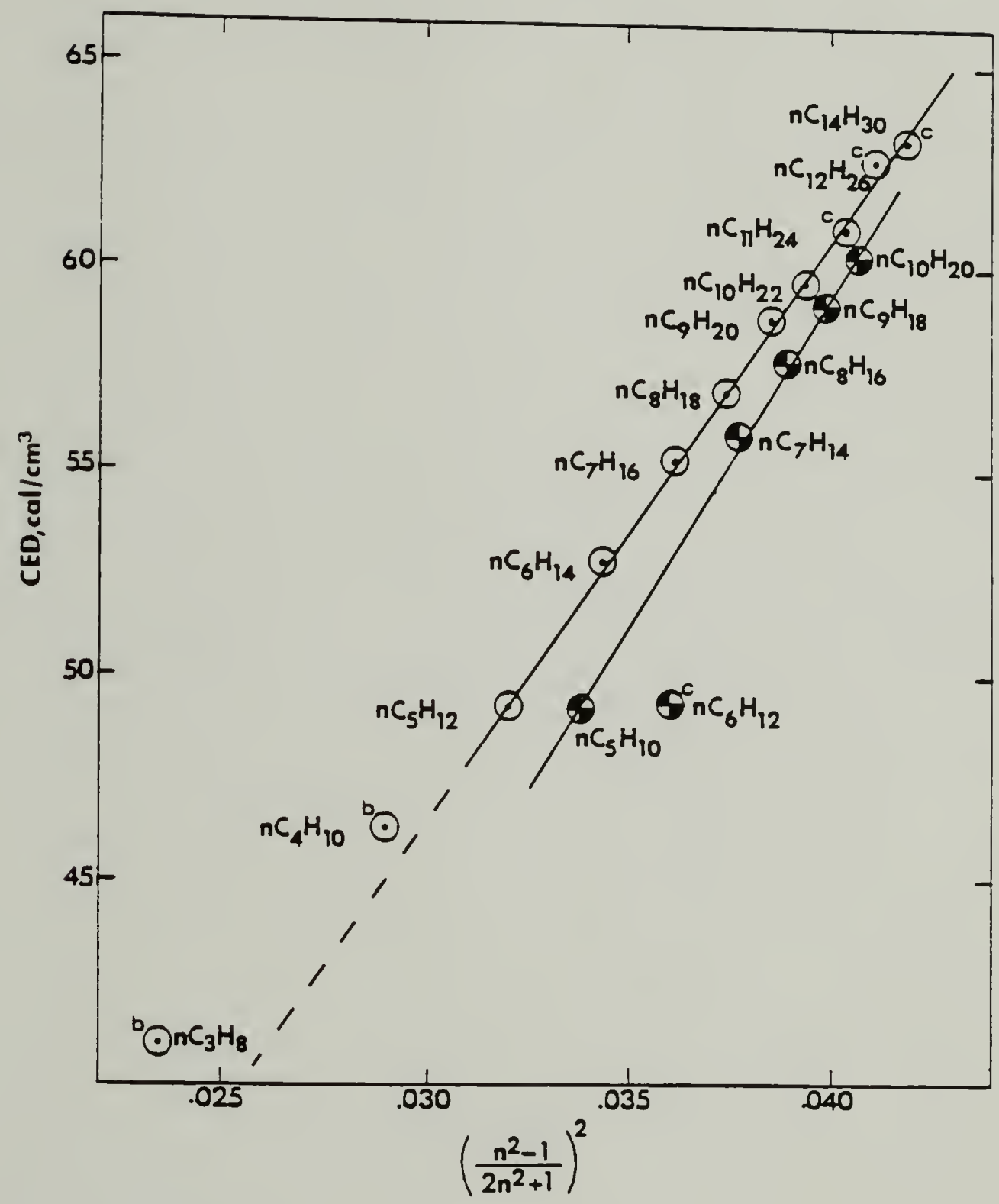

65
60
55
50
45
CED, cal/cm³
nC14H30
c
c
nC12H26
nC11H24
c
nC10H20
nC10H22
nC9H18
nC9H20
nC8H16
nC8H18
nC7H14
nC7H16
nC6H14
nC5H12
nC5H10
c
nC6H12
b
nC4H10
b
nC3H8
.025
.030
.035
.040
(n²−1 / 2n²+1)²

Fig. XIII-2. Change of CED with g^2 for methyl-n-alkyl ketones (△) and n-alkyl benzenes (▲) at 25°C; superscript corresponds to that in Table XIII-1.

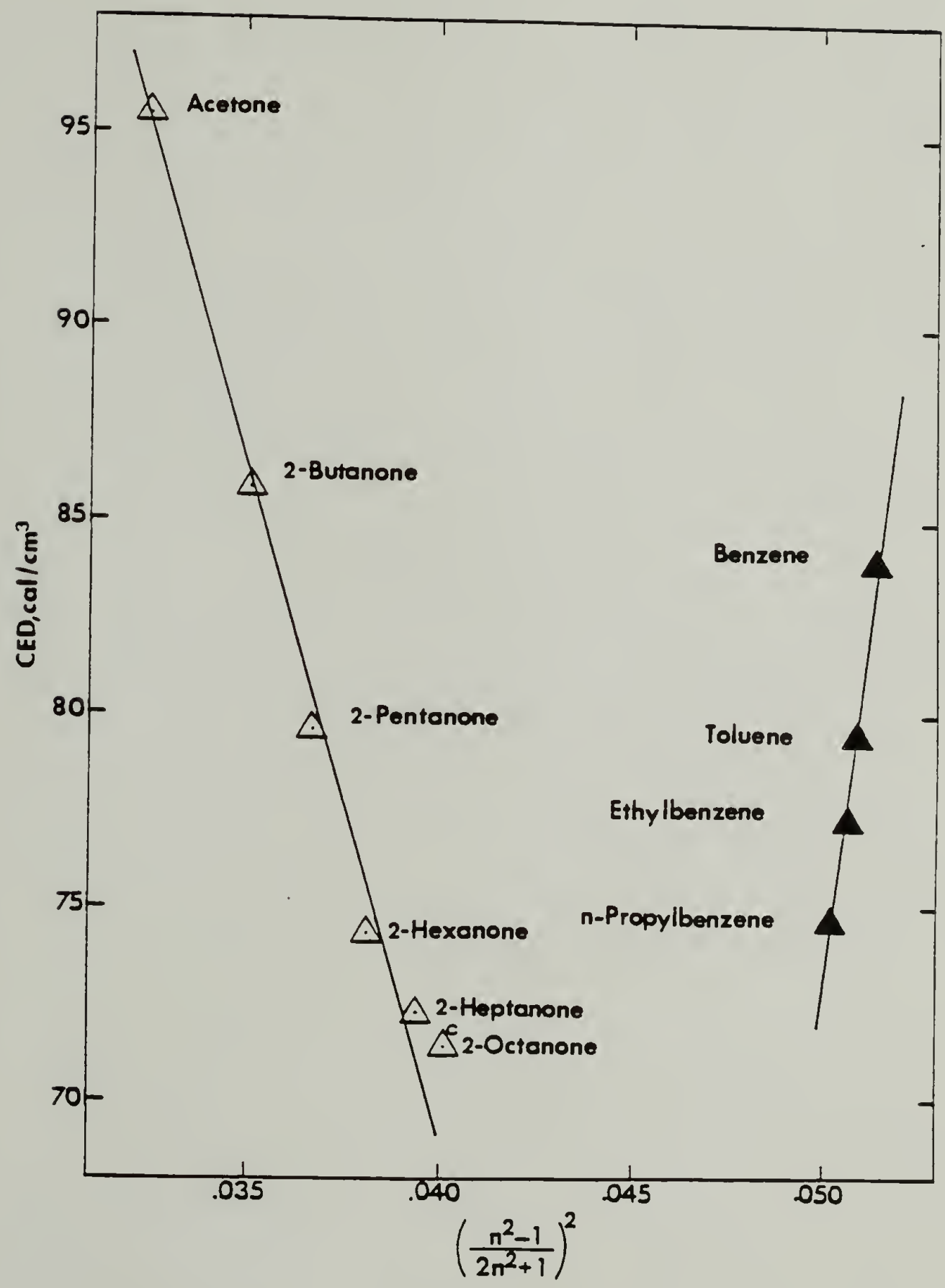
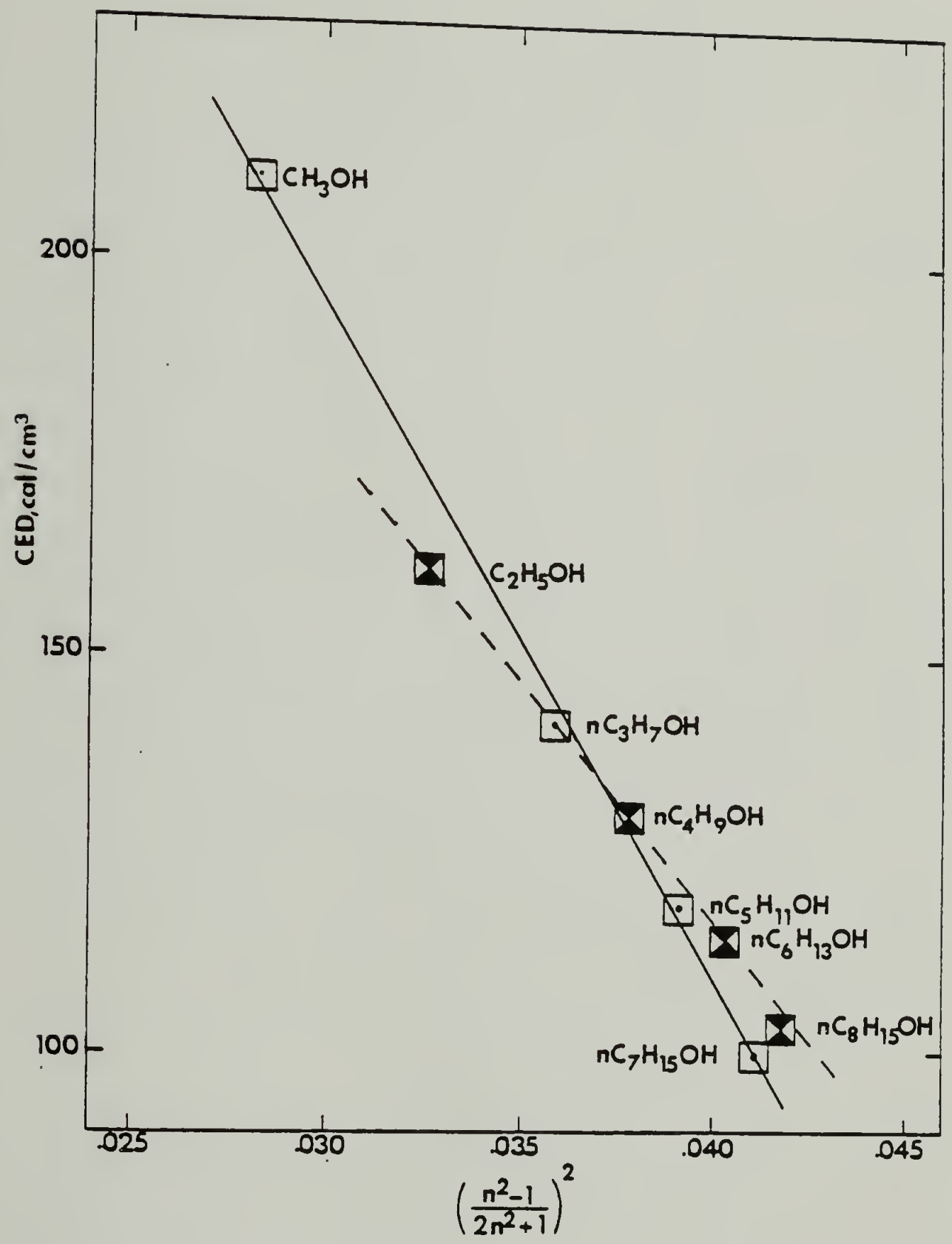

Acetone
2-Butanone
2-Pentanone
2-Hexanone
2-Heptanone
2-Octanone
Benzene
Toluene
Ethylbenzene
n-Propylbenzene
95
90
85
80
75
70
CED, cal/cm³
.035
.040
.045
.050
$\left(\frac{n^2-1}{2n^2+1}\right)^2$

Fig. XIII-3. Change of CED with g^2 for linear alcohols with odd (□) and even (⊠) number of carbons.


CH3OH
C2H5OH
nC3H7OH
nC4H9OH
nC5H11OH
nC6H13OH
nC8H15OH
nC7H15OH
200
150
100
CED,cal/cm3
.025
.030
.035
.040
.045
(n2−1 / 2n2+1)2

$$g^2 = \left(\frac{n^2 - 1}{2n^2 + 1}\right)^2 \qquad \text{(XIII-5)}$$

For n-alkanes (Fig. XIII-1) CED is proportional to g^2. Experimental points for alkanes of low molecular weight deviate from the correlation. The upward orientation of this devation suggests that it may be caused by the errors in determining the small enthalpies of evaportion for those compounds. Assuming that polyethylene, PE, is ideally linear, the observed linear dependence of CED on g^2 for n-alkanes can be extrapolated to the g^2 value for PE. Literature contains different values of n for PE. Using values from two sources, g^2 has been calculated as 0.050 (31) and 0.053 (32). Extrapolating liner dependence of CED on g^2 for n-alkanes corresponding values of CED for PE are 75.5 and 79.2 cal/cm^3, respectively. These values are 13 to 27% higher than reported experimental results (62 to 66 cal/cm^3) (9,32).

The agreement between the extrapolated and experimental CED may be considered acceptable for an extrapolation based on a single material parameter, and on a series of only six n-alkanes between pentane and decane. Higher values for extrapolated CED may be attributed to the simpler structure of short n-alkanes. The size of these differences, however, indicate that the interactions making the main contribution to CED in PE have the same character as in low molecular weight n-alkanes.

For linear 1-n-alkenes (Fig XIII-1) CED is also increasing with g^2. The 1-n-alkenes have both g^2 and CED higher than homomorphous

n-alkanes, yet, their CED are smaller than for imaginary n-alkanes of corresponding g^2, as it can be seen on Fig. XIII-1. Those differences are decreasing with molecular weight.

Similarly, n-alkyl benzenes (Fig. XIII-2) have CED increasing linearly with g^2 with a slope which is much steeper than for n-alkanes. Short chain substituted benzenes have CED values higher than n-alkanes with corresponding g^2 (Fig. XIII-1 and Fig. XIII-2). However, different from the cases of n-alkanes or 1-n-alkenes, both g^2 and CED decrease as the length of n-alkyl segment increases. Interestingly, CED for benzene falls on the same line with other members of the series.

For the polar compounds, methyl n-alkyl ketones (Fig. XIII-2), and linear alcohols (Fig. XIII-3), the CED decrease linearly with g^2. It is noteworthy that separate linear correlations exist for alcohols with an odd and for alcohols with an even number of carbons. Each of the correlations for the polar compounds includes the smallest member of the series: acetone, methanol and ethanol, respectively. In all cases CED decrease with the increase in the size of n-alkyl segments.

Discussion

In several previous works, attempts have been made to correlate CED with easily accessible parameters representing the intensity of ORF. Theoretical findings have suggested the dependence of the enthalpy of evaporation on g (7,23). In our work the best correlation has been obtained when CED was compared with g^2. The remarkable

feature here is that unsubstituted n-alkanes and substituted, polar and nonpolar compounds all show a linear dependence of their CED on the same parameter, g^2. The fact that compounds with small molecules and pronounced dipolar or hydrogen bonding interactions correlate with other members of the series, (Fig. XIII-2 and Fig. XIII-3) is unexpected and requires explanation.

Accepting the homomorphous compound approach (33) the difference in CED between an n-alkane and its homomorph, 1-substituted n-alkane, may be considered a contribution of the substituent to CED. This contribution is usually assessed by comparing the CED of the two homomorphous compounds at equal reduced temperatures (33). Results reported in this work indicate that a new approach is possible for assessing the effect of a substituent on CED. Apparently the effect of the substituent is at least twofold:

(a) For all cases studied here, the introduction of the substituent increases considerably the value of the ORF parameter g^2, over the value for an homomorphous n-alkane, and even more over the value for an n-alkane with an equal number of carbon atoms. It has been demonstrated for a nonpolar molecule in polar solvents (34) and vice versa (29) that ORF is a good representative of the total electric field on the solute. The intensity of purely dispersive, nonspecific, intermolecular interaction between a 1-substituted n-alkane and the continuum may thus be expected to be equal to the intensity of interaction between its homomorphous n-alkane and the medium of equal g^2. In the first approximation it may be equated to the inter-

molecular interaction between one molecule and the continuum in pure n- alkane with the same g^2. Thus the contribution of purely dispersive interaction to the total CED at 25°C corresponds to the CED of an imaginary n-alkane with g^2 equal to that of the substituted compound.

(b) The substituent may enter in specific intermolecular interactions (2-5,29,30). This increases CED and is reflected in the difference between CED of the substituted n-alkane and the imaginary n-alkane with equal g^2. In this work the contribution of intermolecular interactions, other than dispersive to CED of methyl-n-alkyl ketones at 25°C are 2 to 18% higher than values reported earlier for the same set of compounds and for tempratures at which their vapor pressure is 100 mm Hg (35).

For n-alkanes, 1-n-alkenes and n-alkyl benzenes the intensity of CED increases with the rise of g^2. This is in an agreement with the assumption that those compounds interact only through dispersive interaction. For n-alkanes, this indicates also that all the molecular parameters determining the intensity of interaction of the molecule with the field are independent of molecular weight. This in turn implies that the methylene group is the structural unit involved in intermolecular interaction. In the case of 1-n-alkenes the vinyl group enhances g^2 but at the same time CED is below that of an imaginary n-alkane with equal g^2. This difference is smaller for longer molecules. A possible explanation may be associated with the density reduction due to the stiff vinyl group. The change of CED with g^2 for benzene and n-alkyl benzenes suggests that the character of inter-

molecular interaction may not be purely dispersive as customarily assumed, or that the aromatic ring sensitizes the compound to the effect of ORF. Following this argument it will be interesting to see whether the higher members of the series will have CED below the level of n-alkanes with the corresponding g^2. The lack of experimental values for their evaporation enthalpies prevents, however, a further analysis.

Both alcohols and ketones show the decrease of CED with the increase of g^2. For alcohols the fraction of CED above the dispersive interaction may be attributed to the hydrogen bonding (1,30). For ketones it may be attributed to strong dipole-dipole interactions (1,28,29). In both cases it may be noticed that this decrease follows the increase in the molar volume, i.e. the decrease of the equivalent concentration of groups able to enter in specific interactions. Assuming the validity of the isomorphous concept this indicates that only the contribution of the specific interactions to total CED decreases as the size of the n-alkyl segment increases.

Conclusions

1. For nonpolar n-alkanes and for both nonpolar and polar 1-substituted n-alkanes, the CED within an homologous series is found to change linearly with a single material parameter, $g^2 = [(n^2 - 1)/(2n^2 + 1)]^2$, reflecting the intensity of the Onsager reaction field, ORF.

2. For n-alkanes, the dependence of CED on g^2 can be extrapolated to the g^2 for the limiting member of the series, PE. CED obtained

this way for two g^2, both based on values of n reported in the literature, are in fair agreement with experimentally determined CED for commercially produced, branched PE.

3. The presence of either an electron-rich or a polar substituent increases the intensity of ORF and thus increases the intensity of purely dispersive interaction for the substituted n-alkanes above the level of the homomorphous n-alkanes.

4. Polar groups, as substituents, cause CED to rise above the level for n-paraffins with corresponding g^2. For alcohols, this increase is attributed to the hydrogen bond and for ketones to dipole-dipole interaction. The relative contribution of specific interaction to CED decreases as the size of the molecule increases.

5. Vinyl groups, as substituent, depresses the CED below the level for n-alkanes of equivalent g^2. A possible explanation may be related to the increse in the molar volume of the liquid due to the stiff vinyl group.

6. Phenyl ring, as substituent, causes a strong increase in both g^2 and in CED for short chain n-alkyl benzenes. However the effect of phenyl ring on CED requires further experimental and theoretical analysis.

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C H A P T E R XIV

THERMAL DEGRADATION OF POLY(ORTHO CHLORO STYRENE)

Introduction

In a span of more than forty years, probably the most often studied case of polymer thermodegradation was that of polystyrene (PS) (1-6). Meanwhile the study of substituted polystyrenes was not as intensive. Some polystyrenes with α and β substituents were studied either independently, as was poly(α-methyl styrene) (4), or as a part of PS degradation studies (3,4,9). Among polystyrenes with substituent on the ring, only poly(amino styrenes) are studied in greater detail (7). Also, some data can be found concerning poly(meta methyl styrene) (3,4,8). It appears that there is only one study of the thermodegradation of poly(para methoxy styrene), poly(para methyl styrene), poly(para chloro styrene), PPClS, and poly(para bromo styrene), PPBrS (10). In that study properties of those four polymers were compared and related to the inductive character of the substituent.

The effect of the chlorine on the chemical and physical properties of ortho chloro styrene, OClS, and poly(ortho chloro styrene), POClS, has already been studied (11-15). The results may be summarized as follows:

(a) Chlorine as a substituent acts as an electron withdrawing agent. Thin induces polarization of the double bond as well as of the αCH bond (11).

(b) Chlorine acts as a resonance electron donor. This induces a resonant stabilization of any chloro styrene free radical. In the case of POClS this is further enhanced due to the ortho position of the chlorine. Because of this the POClS radical is more stable than the free radical of PS (11,12).

(c) Chlorine in ortho position hinders both the oscillation of the phenyl ring and the conformational motion of the POClS chain.

As a result, some characteristics of the OClS polymerization are altered with respect to styrene polymerization. It has been shown that in the succession of POClS, PS, and PPClS, the tendency of the free radical to act as an electron donor weakens, while the tendency toward the abstraction of the hydrogen from the substrate increases (12). Accordingly, in a polymerization initiated with benzoyl peroxide, at 60°C, OClS polymerizes twice as fast as styrene. Whereas, in the thermal polymerization, rates for OClS, para chloro styrene, PClS, and styrene are in the ratio 10.7:4:1 (13).

Reduced conformational mobility of POClS, relative to PS, was reflected in the increased glass transition temperature (1.07 times), (14,18), steric factor, σ, (1.08 times) (14), and critical chain length for entanglement, (1.22 times) (15).

The thermal degradation of POClS has not yet been studied. It is the intent of this study to investigate characteristics of this process and to find effects which are possibly resulting from the presence of the chlorine in ortho position.

Experimental

Materials and sample preparation. The OClS was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. It was polymerized in toluene with azobisizobutyronitrile, AIBN, as the initiator (15,16,17,18). The reaction mixtures were flushed with nitrogen and polymerized in sealed glass containers at 60 ± 2°C. The polymer was precipitated twice in methanol. Two different molecular weights of POClS were obtained in this manner (Table XIV-1). In addition, anionically polymerized PS, with a narrow molecular weight distribution, was used. This polymer was purchased from Pressure Chemicals Company, Pittsburgh, PA.

Samples for the thermogravimetric analysis were made from 150 - 200 μm thick film, as rectangles weighing 10 ± 1 mg. Films were prepared by pressing under nitrogen at 130°C for PS and 150°C for POClS. During the pressing the total time of exposure to high temperature did not exceed 3 minutes.

In order to study changes in molecular weight, samples were prepared in the following manner: 10 mg of polymer was placed in a norrow (3 mm i.d.) glass test tube and dissolved in 0.1 ml toluene. The solution was deaerated, by alternating low vacuum and nitrogen pressure, and then dried at low vacuum. The thin films formed this way were dried for an additional 48 hours at 85°C and 10^{-3} mm Hg. After cooling, the tube was flushed three times by alternating vacuum of 10^{-5} mm Hg and oxygen-free nitrogen. Finally, the tube is sealed

Table XIV-1

Molecular Weights of Polymers Used in the Thermodegradation Experiment

Polymer Designation	M_v	M_w	M_n	M_w/M_n
POC1S-1	101,300	115,500	60,700	1.91
POC1S-2	379,000	317,500	154,800	2.05
PS	390,000	420,600	370,000	1.14

at 700 mm Hg of oxygen-free nitrogen.

Experimental Techniques

Pyrolysis-gas chromatography. The pyrolysis was performed using two different techniques. A Chromolytic Multi-Purpose Thermal Analyzer, Model MP-3 was used for tests at 300°C. The procedure comprised heating 0.8 - 1.0 mg of powdered polymer (in a quartz boat) under helium stream for 5 minutes. Products of the degradation were collected at liquid nitrogen temperature and subsequently evaporated at 300°C into the gas chromatograph. In the second procedure, used for tests at 700°C, a filament pyrolyzer attached to a gas chromatograph was equipped with 6' x 1/8" column with 5% Dexil 300 on Chromosorb 750, and with a flame ionization detector. The column was heated between 50° and 300°C at 10°C/min and held at 300°C for an additional 60 minutes.

Thermal degradation. A DuPont Thermogravimetric Analyzer, Model 900, was used to record the weight loss of the polymer as a function of time, temperature, and atmosphere. The flow of the purging gas (oxygen-free nitrogen or air) was adjusted to 6 ml/min.

Controlled isothermal degradation was performed by exposing the samples in sealed tubes to the desired temperatures for a given length of time. For the degradation at 150°, 200°, and 250°C, an oil bath with a temperature stability of ± 1°C was used. For the tests at 300°C a furnace was used with a temperature stability of ± 3°C.

Degradation was performed on several samples (up to 8) for each condition; average values and variations are reported.

Determination of molecular weights. Molecular weights of undegraded POClS were determined viscometrically using the Mark-Houwink equation established by Matsumura (15) for the solution in toluene at 30°C.

A Gel Permeation Chromatograph, GPC, was used to determine molecular weights for both undegraded and degraded polymer samples. The instrument used was a Waters Associates GPC Model 200 equipped with μ-Styra-gel columns with nominal pore sized 10^7, 3×10^5, 3×10^4, and 3×10^3 Å. The solvent was tetrahydrofuran (THF) at a flow rate of 1 ml/min at 25°C. The polymer concentration was 10 mg/ml. The GPC was calibrated using PS standards from Pressure Chemicals Co., Pittsburgh, PA.

The Mark-Houwink equation for POClS in THF is not known, and only apparent molecular weight averages have been determined on GPC calculating MW for POClS as if it were PS. The apparent molecular weight averages for non-degraded samples of POClS show a correlation with the corresponding viscosity average molecular weights. Therefore, the relative changes in the apparent M_w and M_n, as determined on GPC, can be taken as relative changes of absolute M_w and M_n of the POClS.

Results and Discussion

Pyrolysis-gas chromatography. Pyrolysis of PS under helium at 300°C yields, in the first 5 minutes, a mixture containing at average 17% of monomer and volatiles of higher molecular weight. Pyrolysis of POClS under identical conditions, yields a mixture containing 95% of monomer with volatiles of higher molecular weights. At 700°C the volatiles contain only the monomer, OClS. These results for POClS correspond to the results obtained from the pyrolysis of PPClS for 5 sec at 434°C and 690°C where the yield was 85% and 100% of monomer respectively (10). Similarly the pyrolysis of PPBrS at 434°C and 690°C yields 94.5% and 100% of monomer respectively (10).

The high concentration of the monomer in the volatiles indicates that intramolecular chain transfer in POClS is greatly reduced relative to PS (25). This is in agreement with the character of the POClS free radical, which is more stable, and less prone towards hydrogen abstraction, than the PS radical. By analogy the intensity of the intermolecular activity transfer which would yield shorter chains is also expected to be smaller for POClS than for PS.

Thermogravimetry under nitrogen. During isothermal degradation under nitrogen (Figure XIV-1) POClS exhibits a slower weight loss than PS. Since the change in molecular weight under the same conditions (Figure XIV-4) indicates a larger number of chain scissions for POClS than for PS, this slow weight loss indicates that the depolymerization of POClS

Fig. XIV-1. Isothermal degradation under nitrogen. Relative changes in weight of PS(▽200°C, △ 250°C, □ 275°C, ○300°C) and POCl$_3$-2 (▼200°C, + 220°C, ▲250°C, ■ 275°C, ●300°C).

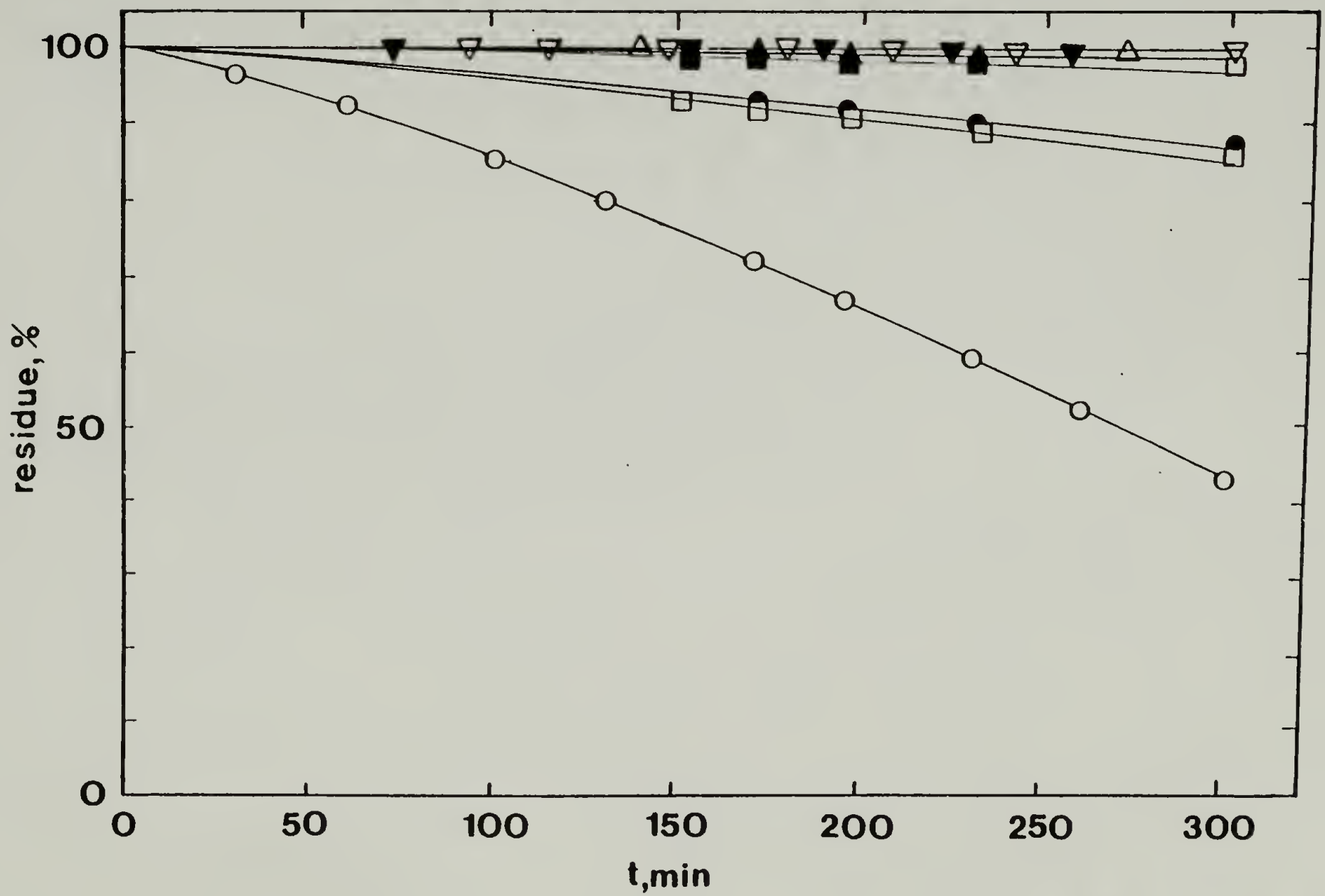

100
50
0
residue, %
0
50
100
150
200
250
300
t,min

Fig. XIV-2. Isothermal degradation in air. Relative changes in weight of PS (▽ 200°C, △ 250°C, □ 275°C, ○ 300°C) and POC1S-2 (▼ 200°C, + 220°C, ▲ 250°C, ■ 275°C, ● 300°C).

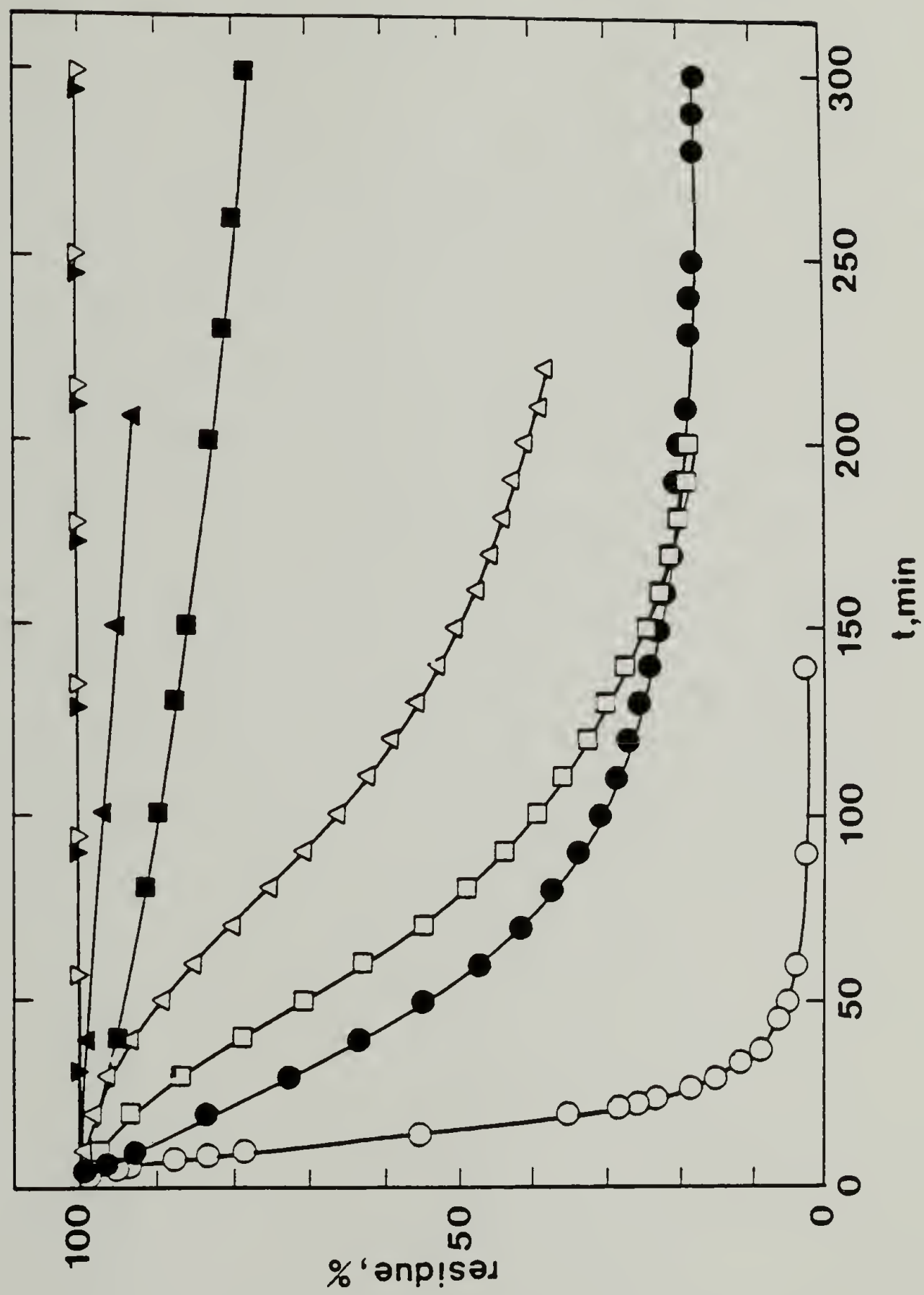

residue, %
100
50
0
0
50
100
150
200
250
300
t,min

Fig. XIV-3. Thermal Degradation at heating rate 5°C/min. The change of weight for PS and POClS in air (---) and under nitrogen (——).

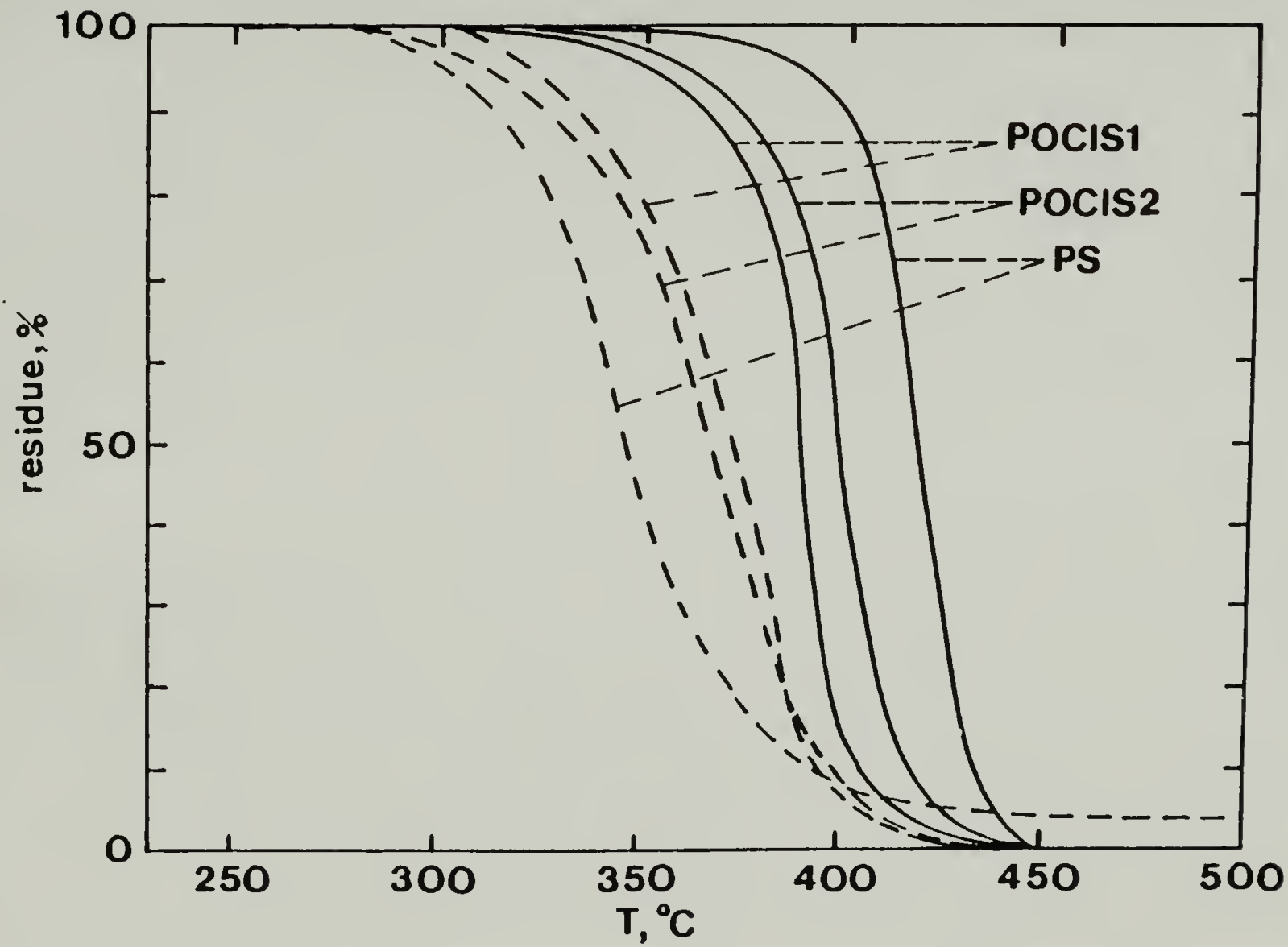
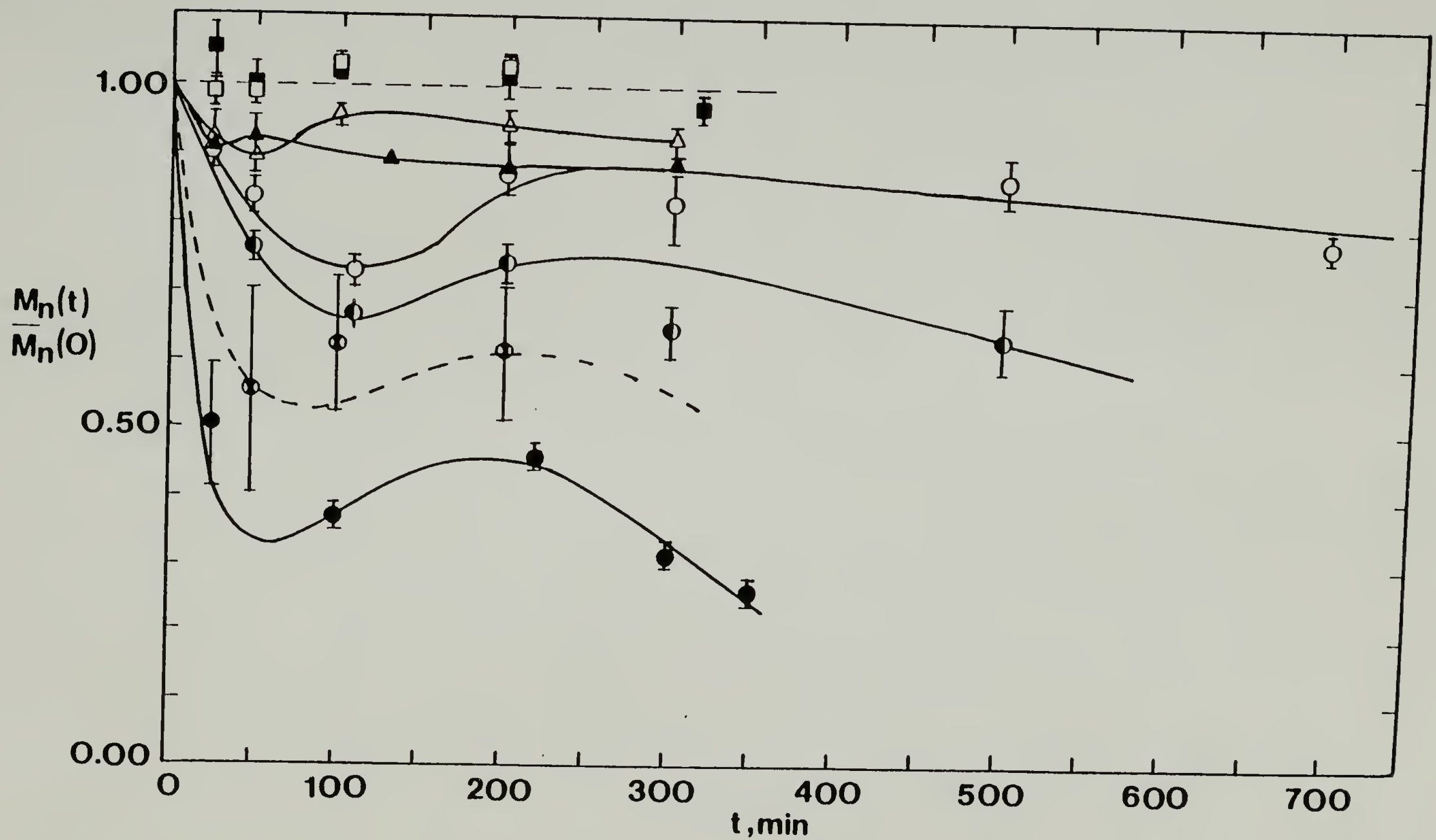

100
50
0
residue, %
250
300
350
400
450
500
T, °C
POCIS1
POCIS2
PS

Fig. XIV-4. Isothermal degradation under nitrogen. The change of molecular weight of PS (□ 200°C, ■ 250°C); POCl$_3$S-1 (△ 200°C, ▲ 250°C) and POCl$_3$S-2 (○ 150°C, ◑ 200°C, ⊗ 250°C, ● 300°C).


1.00
0.50
0.00
$\frac{M_n(t)}{M_n(0)}$
0
100
200
300
400
500
600
700
t, min

is considerably slower than that of PS. This may be attributed to: (a) high stability of the POClS free radical and (b) greater activity of the OClS monomer, having a polarized double bond (12), toward the electron-donating free radical (11). The temperatures at which occurs weight loss of 50%, at different heating rates, (Table XIV-2), indicate that the thermostability of both POClS and PS depends on the rate of heating. However, POClS is more sensitive to the heating rate. The thermostability of POClS exceeds that of PS at heating rates slower than approximately 2°C min, while above this heating rate its thermostability is lower (Figure XIV-3). Since results from isothermal tests suggest slower depolymerization of POClS, the constant heating rate experiments indicate a more pronounced chain scission of POClS at higher heating rates. The fact that the polymer with a stiffer chain exhibits more chain scission at higher heating rates suggests that the relaxation properties of the polymer may be of critical importance during thermal degradation.

The activation energies for the thermodegradation under nitrogen were determined using relation (1) derived by Reich and Stivala (20).

$$E_{dc} = \frac{-R}{0.456} \cdot \frac{dv_h}{d(1/T_{dc})} \text{ [kcal]} \qquad (1)$$

where E_{dc} is the energy of activation at some constant degree of conversion, T_{dc} is the absolute temperature at which this degree of conversion is reached at the heating rate v_h, and R is the universal

TABLE XIV-2

Thermodegradation Under Nitrogen

Effect of the Heating Rate on the Characteristic Temperature T_{50} for PS and POC1S

Heating Rate, °C/min	T_{50}, °C	
	POC1S-2	PS
1	377	374
2	397	403
5	400	420
10	422	430
20	440	452

gas constant. This relation, based on different heating rates, does not require any assumptions concerning the order of the reaction during the degradation process. The temperatures T_{dc}, for the conversions of 20, 50, 70 and 90% were determined at heating rates of 1, 2, 5, 10 and 20°C/min. The activation energies for different conversions did not differ significantly. For POClS the average value is $\overline{E}_{dc}$ = 39.7 ± 0.7 kcal/mole. For the PS the average value is $\overline{E}_{dc}$ = 27.3 ± 0.6 kcal/mole. The value for the activation energy for thermodegradation of POClS has not previously been reported. Values reported for PS vary considerably, depending primarily on the approach used to interpret the data. Some of the reported values are 27.0 (23), 28.0 (22), 44.0 (22), 44.7 (22), and 57.0 kcal/mole (4,21).

Change in the molecular weight. PS exposed to 200 or 250°C under oxygen-free nitrogen does not show any change in molecular weight (Figure XIV-4). POClS-1 and POClS-2 exposed to 150, 200, 250, and 300°C, under oxygen-free nitrogen, show unique changes in molecular weights (Figures XIV-4). These changes occur in a process which may be divided into three distinct periods:

(a) initial period corresponding to a pronounced decrease in molecular weight;

(b) second period characterized by a partial recovery of molecular weight; and

(c) third period exhibiting a slower decrease in molecular weight.

(a) Initial period. The decrease in molecular weight during this period (Figure XIV-4) is very sharp for the high molecular weight polymer. The change is large at higher temperatures. The conversion to volatiles during this period is either non-measurable (at 150 and 200°C) or very small (approximately 0.1% at 250°C and 0.3% at 300°C). The change is similar in nature, but much higher intensity, than the change in molecular weight for PS at 300 to 340°C and at conversions to volatiles of 5 -10% (5,6,16,17).

For POClS of lower molecular weight the decrease is very small. However, the intensity of the change shows the same correlation with temperature (Figure XIV-4). Smaller relative decrease of molecular weight has also been reported for PS (2,26,27). The proportionality between the intensity of degradation and molecular weight of the polymer can be related to slower relaxation of the higher molecular weight polymer. Since POClS has a stiffer chain and longer relaxation time, it would be expected to be more susceptible to degradation than PS. This is in agreement with our results for PS and POClS of similar molecular weights.

(b) Second period. Between the 50th and 200th minute, an increase in molecular weight is observed for both samples of POClS (Figure XIV-4). For POClS-2 this increase represents a recovery of 15% at 300°C and of 50% at 150°C. For the sample of lower molecular weight, POClS-1, it is more difficult to estimate the recovery but the trend is similar. This kind of secondary increase of molecular weight,

during the degradation of a linear polymer in bulk, has not previously been reported. An increase in molecular weight for PS in dilute toluene solution at 250°C and 280°C has been reported (19). However, since the physical conditions were considerably different, a parallel can not be drawn between these two studies.

The experimental results for POCl3 suggest that these unique results are the consequence of an inverse gel effect occurring during thermal degradation. The process can be explained as follows: The resonant stabilization and the highly viscous medium cause a considerably longer activity of the free rdicals than in PS melt or in solution. This results in a continuous increase of the free radical concentrtion during the first period of the degradation. When certain favorable conditions, consisting of low viscosity and high free radical concentration, are reached the recombination rate starts to increase sharply. This results, in the second period, in a relatively strong increase of molecular weight. If this mechanism is correct one may expect that at lower temperatures:

(a) smaller number of free radicals will be formed

(b) once formed, free radicals will have lower energy and smaller tendency towards depolymerization; and

(c) free radicals will have smaller mobility and thus a smaller chance for deactivation through disproportionation or recombination. This would result in:

(a) smaller weight loss; and

(b) a larger relative recovery of molecular weight through recombination.

Both of these estimates are in agreement with our experimental results.

The concept of macroradical recombination was first introduced by Wall and coworkers (26,27) to explain the change in molecular weight distribution during the thermodegrdation of PS. The assumption was that the activity of PS free radical was maintained through a succession of intermolecular activity transfers. One may assume that a similar mechanism exists during thermodegradation of POClS. However, at least two facts indicate the contrary. First, as it has been shown earlier, the activity transfer is of minor importance for POClS. Second, if an increase in activity transfer rate occurs at lower temperatures, this would result in a larger number of short chains per one active macroradical. Consequently, relative recovery of molecular weight would be smaller at lower temperatures. This is opposite to the experimental results.

Long-chain grafting appears to be a highly unlikely mechanism for the increase of molecular weight of POClS. The reason for this is the high sterical hindrance which would exist in all possible structures which might be formed through grafting.

(c) Third period. In the third period, samples of lower molecular weight show an insignificant change in molecular weight (Figure

IXV-3). The value of M_n approaches an assymptote of 53,000 at 200°C and an assymptote of 51,000 at 250°C. In spite of the fact that a PS calibration curve is used for the determination of M_n, these values are noticeably near the critical entanglement molecular weight for POClS which is 57,000 (15). For the higher molecular weight polymer the decrease of molecular weight is slower than in the first period. In addition the intensity is found to be temperature dependent. This change resembles the secondary, linear, decrease of molecular weight seen in the degradation of PS at 300 to 340°C (5,6).

The average values for M_w/M_n were determined from GPC data for all degraded samples of POClS (Table XIV-3). For the high molecular weight sample a broadening of the molecular weight distribution occurs in the first period. This broadening is more pronounced at higher temperatures. In the second and third period both leveling off and narrowing of the distribution occurs. However, the trend is not clear since the changes at different temperatures differ in direction. For the low molecular weight sample the relative changes of M_w/M_n are below the level of the experimental error.

Several of the experimental results suggest that degradation of POClS occurs through scission of weak links: When the Scott's criterion (24) is applied, majority of experimental points fall in the domain which would indicate random scission of polymers with initial values of M_w/M_n between 1.0 and 1.5. Even if the apparent value for $M_w/M_n = 2.05$ is erroneous, the difference in the results is large

Table XIV-3

Effect of the Atmosphere on Thermodegradation

Average Values for the Characteristic Temperatures T_{50}, under N_2 and Air, for PS and POClS at Heating rate 5°C/min

Polymer	T_{50} (N_2), °C	T_{50} (air), °C	Difference, °C
POClS	392	368	24
POClS-2	400	372	28
PS	420	347	73

enough to suggest a nonrandom scission. The difference in the intensity of the molecular weight change at different temperatures, and for different initial molecular weights, as well as the leveling off of the molecular weight at values near the critical value for entanglement, also rule out random scission. The rate of weight loss at 150° and 200°C is practically zero while the molecular weight change is very pronounced. Also at 250° and 300°C the weight loss rate stays constant while the new chain ends are formed and neutrlized. This implies that even if scission occurs, not all the free radicals formed are active enough to undergo depolymerization.

The weak links that break first are either structural inhomogeneities which interfere with the thermal motion, or bonds, in the entanglement complex, which are already strained due to the intramolecular interferences. The scission of the chemically weak links, specifically, peroxy groups, appears the most obvious explanation but it, however, seems to be contradictory to experimental results. This kind of scission would create a large number of inactive chain ends, having higher relative concentration at lower temperatures. This, in turn, would result in a smaller relative recovery of molecular weight at lower temperatures.

Thermogravimetry in air. At higher tempertures both POClS and PS are sensitive to the presence of oxygen. However, the reactivity of PS with oxygen is considerably higher than that of POClS. This can be seen comparing the rates of the weight loss of the two polymers under

nitrogen and in air at constant heating rate (Figure XIV-3 and Table XIV-3). The lower activity of POClS toward oxygen may be explained as a consequence of the αCH bond character. This bond is polarized and electron-deficient. Consequently, it is less active toward an electrophylic substituent, such as oxygen, than a corresponding bond of PS. The nonvolatile residue of PS degraded in air is at average 2.5%, both at constant heating rate (and 500°C) (Figure XIV-3) and under isothermal conditions (after 270 min at 300°C) (Figure IXV-2). This residue may indicate some oxidative crosslinking. The quantities of residue from our experiments were too small for solubility test or elemental analysis.

POClS does not have a residue at constant heating rate (Figure XIV-3). However, at 300°C in air, after 300 min 17% still remains unvolatilized (Figure XIV-2). The elemental analysis of this residue shows less than 1% difference from the theoretical content of C, H, and Cl in POClS. If this difference is (within the experimental error) considered to be oxygen, it would represent one peroxy group per 28 repeating units. The residue is completely soluble in toluene at room temperature, which indicates the absence of excessive crosslinking.

Conclusions

The thermal and thermooxidative properties of POClS, differ considerably from that of PS. This can be explained by the known effects of chlorine or the properties of the monomer and of POClS free radical

as well as on the chain mobility.

1. The unique pattern in the molecular weight change, the partial recovery of the molecular weight following the initial decrease, may be explained by the high resonance stability of the free radical and by its low tendency towards activity transfer through hydrogen abstraction.

2. The pronounced initial decrease in molecular weight, as well as the increasing weight loss at higher heating rates may be due to chain rigidity of POClS. A stiffer chain cannot accommodate thermally induced stress before primary bonds are broken.

3. The low weight loss during degradation is the consequence of both the free radical stability and monomer activity. In equilibrium, even at high temperatures, the polymer is favored over the monomer which would be produced through unzipping.

4. High relative content of monomer, in the volatile products of degradation, may be due to the low tendency of the free radical to undergo the activity transfer by hydrogen abstraction.

5. The weight loss during thermodegradation in air which is lower for POClS than for PS may be a consequence of the electron deficiency of its αC-H bond and, consequently, its lower reactivity towards oxygen.

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APPENDIX

Table A-1

Symbols and Acronyms

No.	Symbol	Compound
1	ACSC6	hexane, Amer. Chem. Soc. Standard Reagent
2	ANIS	methylphenylether
3	BENZ	benzene
4	C5	n-pentane
5	C6	n-hexane
6	C7	n-heptane
7	C8	n-octane
8	iso C8	2,2,4-trimethylpentane
9	C9	n-nonane
10	C10	n-decane
11	C11	n-undecane
12	C12	n-dodecane
13	C13	n-tridecane
14	C14	n-tetradecane
15	C15	n-pentadecane
16	C16	n-hexadecane
17	C_2Cl_4	tetrachloroethylene
18	C_6H_{12}	cyclohexane
19	C_2HCl_3	trichloroethylene
20	C1OH	methanol
21	C2OH	ethanol
22	C3OH	n-propanol

Table A-1, continued

No.	Symbol	Compound
23	C4OH	n-butanol
24	C5OH	n-pentanol
25	C6OH	n-hexanol
26	C8OH	n-octanol
27	C12OH	n-dodecanol
28	2CP	2-chloropropane
29	CUM	cumene
30	CYCLOC6	cyclohexane
31	1,2DBE	1,2-dibromoethane
32	1,2DCE	1,2-dichloroethane
33	2,4DCP	2,4-dichloropentane
34	DEE	diethyl ether
35	DIPB	1,4-diisopropylbenezene
36	DIPE	isopropylether
37	DMF	N,N'-dimethylformamide
38	2,6DMP	2,6-dimethylphenol
39	DMSO	dimethyl sulfoxide
40	DnBE	di-n-butyl ether
41	DnHE	di-n-hexyl ether
42	DnPeE	di-n-pentyl ether
43	DnPrE	di-n-propyl ether
44	DPE (DPhE)	diphenyl ether
45	DPM (DPhM)	diphenyl methane

Table A-1, continued

No.	Symbol	Compound
46	ECL	ε-caprolactone
47	EGDME	ethylene glycol dimethyl ether
48	IPME	isopropyl methyl ether
49	IPrOH	isopropyl alcohol
50	MES	1,3,5-trimethyl benzene
51	p-DIOX	p-dioxane
52	PPO	poly(2,6-dimethyl-1,4-phenylene oxide)
53	$(PPO)_3$	trimer(2,6-dimethyl-1,4-phenylene oxide)
54	PS 600	polystyrene M_w = 600
55	PS 17,500	polystyrene M_w = 17,500
56	PVME(HMW)	poly(vinyl methyl ether) M_w = 139,000
57	PVME(LMW)	poly(vinyl methyl ether) M_w = 14,000
58	TBC	2-chloro-2-methylpropane
59	1,1,1TCE	1,1,1-trichloroethane
60	1,1,2,2TCE	1,1,2,2-tetrachloroethane
61	TETRA	tetrachloroethylene
62	THF	tetrahydrofuran
63	TOL	toluene
64	TRI	trichloroethylene
65	m-XYL	1,3-dimethylbenzene
66	o-XYL	1,2-dimethylbenzene
67	p-XYL	1,4-dimethylbenzene

Table A-2

Corrections for Diamagnetic Susceptibility for 10 vol % p-Dioxane in DMSO-d_6 as External Standard

No.	Solvent	Δδ, ppm
1	ACSC6	-0.27
2	ANIS	-0.09
3	C5	-0.36
4	C6	-0.27
5	C7	-0.28
6	C8	-0.25
7	iso C8	-0.60
8	C9	-0.23
9	C10	-0.22
10	C11	-0.19
11	C12	-0.18
12	C13	-0.17
13	C14	-0.17
14	C15	-0.16
15	C16	-0.16
16	C1OH	-0.36
17	C2OH	-0.30
18	C3OH	-0.24
19	C4OH	-0.21
20	C5OH	-0.19
21	C6OH	-0.17

Table A-2, continued

No.	Solvent	Δδ, ppm
22	C7OH	-0.17
23	C8OH	-0.15
24	C12OH	-0.13
25	2CP	-0.20
26	CUM	-0.13
27	CCl_4	-0.07
28	C_2Cl_4	-0.47
29	$CHCl_3$	0.04
30	C_2HCl_3	-0.47
31	C_6H_6	-0.19
32	C_6H_{12}	-0.18
33	1,2DBE	0.39
34	1,2DCE	0.09
35	2,4DCP	-0.03
36	DEE	-0.36
37	DHE	-0.19
38	DIPB	-0.11
39	DIPE	-0.45
40	DMF	-0.60
41	DMSO	-0.42
42	DnPeE	-0.21
43	DnPrE	-0.30
44	DPE	-0.08

Table A-2, continued

No.	Solvent	Δδ, ppm
45	DPM	-0.06
46	ECL	-0.16
47	EGDME	-0.26
48	IPME	-0.36
49	IPrOH	-0.25
50	MES	-0.11
51	p-DIOX	-0.23
52	TBC	-0.30
53	1,1,1TCE	-0.09
54	1,1,2,2TCE	0.29
55	THF	-0.33
56	TOL	-0.15
57	o-XYL	-0.15
58	m-XYL	-0.20
59	p-XYL	-0.20

Table A-3

Corrections for Diamagnetic Susceptibility for 10 vol % H_2O in DMSO-d_6 as External Standard

No.	Solvent	$\Delta\delta$, ppm
1	ACSC6	0.10
2	C5	0.02
3	C6	0.06
4	C7	0.09
5	C8	0.12
6	iso C8	0.12
7	C9	0.14
8	C10	0.16
9	C11	0.18
10	C12	0.13
11	C13	0.15
12	C16	0.22
13	C10H	0.01
14	2CP	0.17
15	CUM	0.22
16	CCl_4	0.32
17	C_2Cl_4	-0.09
18	$CHCl_3$	0.42
19	C_2HCl_3	-0.08
20	C_6H_6	0.19
21	C_6H_{12}	0.20

Table A-3, continued

No.	Solvent	Δδ, ppm
22	1,2DBE	0.76
23	1,2DCE	0.46
24	DEE	0.02
25	DIPE	-0.07
26	DMF	-0.22
27	DMSO	-0.01
28	DPE	0.30
29	DPM	0.32
30	EGDME	0.12
31	IPME	0.02
32	MES	0.27
33	TBC	0.08
34	1,1,1TCE	0.47
35	1,1,2,2TCE	0.67
36	THF	0.05
37	TOL	-0.18
38	o-XYL	0.22
39	m-XYL	0.18
40	p-XYL	0.18

Table A-4

Corrections for Diamagnetic Susceptibility for Benzene as External Standard

No.	Solvent	Δδ, ppm
1	C6	-0.08
2	C7	-0.09
3	C9	-0.04
4	C10	0.00
5	C16	0.00
6	2CP	-0.02
7	p-DIOX	-0.04
8	TBC	-0.11
9	THF	-0.14